Catalysis Science & Technology

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/d6cy00010j

Base-free reduction of ketones using a bpy-iridium catalyst, focusing on the synthesis of γ-valerolactone

Liwei Guo, Zilong Li, Rémi Marchal, Boris Le Guennic and Cédric Fischmeister *

Received 5th January 2026,
Accepted 28th March 2026

DOI: 10.1039/d6cy00010j

rsc.li/catalysis

Several [Cp*Ir(N∩N)SO_4] complexes have been prepared and used for the efficient reduction of various ketones in water without any additives, using formic acid as the hydrogen donor. The best catalyst incorporating a bis-dimethylaminopyridine ligand was further used for the base-free reduction of levulinic acid into γ-valerolactone (GVL). This catalyst loaded at 0.1 mol% and used under neat conditions led to quantitative conversion of levulinic acid at 30 °C.

The reduction of carbonyl compounds is a ubiquitous reaction in organic synthesis. In particular, the catalytic reduction of ketones into alcohols has found a number of applications in the pharmaceutical, agrochemical, flavour, fragrance, materials, and fine chemical industries. Of particular interest is stereoselective reduction of ketones into chiral alcohols.[1] Reduction reactions using molecular hydrogen or transfer hydrogenation using hydrogen donors have been extensively used in homogeneous catalysis, most often using basic additives or basic media which are necessary for catalyst turnover.[2] However, these basic additives present a number of drawbacks such as strong environmental impact due to waste generation and base removal processes. The limitation to substrates and/or products stable under basic conditions is also a major problem. Finally, the ability of many bases to promote the reduction of ketones without any catalyst is very often overlooked, despite being clearly and unambiguously highlighted in a number of reports.[3] The reactivity of certain bases is particularly problematic when the stereoselective reduction of ketones is targeted. For these reasons, in the past years, researchers have been investigating organometallic catalysts able to promote the reduction of ketones without any assistance of basic additives. This challenge is addressed using a catalyst able to play the dual role of a catalyst and base through metal–ligand cooperation or using catalysts incorporating basic ligands or hydrides.

In fact, catalysts able to reduce ketones under base-free conditions are not many. Following the pioneering work by Shvo in 1985,[4] only few catalysts operating under base-free conditions have been reported. Noyori addressed the issue of base-sensitive ketones and reported a *trans*-RuH(η^1-BH_4)(binap)(1,2-diamine) catalyst for the base free hydrogenation of simple ketones followed by examples of hydrogenation of base sensitive chromanone[5] and chloroacetophenone derivatives[6] with high enantioselectivity. Among the base-free reduction of ketones, hydrogenation transformations have been the most reported displaying, in several cases, high activity under mild conditions. In 2012, Milstein reported a P,N,P-pincer iron-hydride complex that catalysed the hydrogenation of ketones in ethanol at 4.1 bar and 40 °C in 6 h.[7] At the same period, Hanson reported various cobalt-pincer complexes for the hydrogenation of olefins and ketones. Interestingly, a cobalt catalyst (2 mol%) bearing a basic alkyl ligand $-CH_2SiMe_3$ effectively hydrogenated acetophenone under very mild conditions (1 bar, 25 °C) in dry THF, but no substrate scope was provided.[8] Two ruthenium-containing phosphine sulfonate chelate catalysts (2 mol%) were reported by Achard and Bruneau for the hydrogenation of aryl-ketones.[9] Very high yields were achieved at 60 °C and 30 bar. Deng also reported a series of *N*,*O*-chelate half-sandwich ruthenium complexes (0.1 mol%) for both carbonyl and nitro compound hydrogenation under mild conditions (5 bar, 50 °C) in a methanol/water mixture.[10] In 2019, Xing's group developed Cp*–iridium complexes (0.5 mol%) hydrogenating a broad scope of ketones and aldehydes under mild conditions (1 bar, 30 °C).[11] It must be mentioned that the stereoselective hydrogenation of aromatic ketones was reported by Andersson using a high loading of a cationic iridium complex (1 mol%) at room temperature and 1 bar H_2 in iPrOH.[12] Recently, Kirchner reported a Mn(I)–diphos complex catalysing the hydrogenation of aryl- and alkyl-ketones in high yields at room temperature and 10 bar H_2 in Et_2O with 3 mol% catalyst loading.[13] Similarly, only a few catalysts have been reported for the base-free transfer

Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes), UMR 6226, F-35042 Rennes, France. E-mail: cedric.fischmeister@univ-rennes.fr

hydrogenation of ketones using i-PrOH as a hydrogen donor since the 80's,[14] involving metal-hydride catalysts[15] and other ligands.[16] Examples of base-free reduction of ketones using formic acid (FA) as a hydrogen donor are even more scarce. It appears that Watanabe likely published the pioneering work on base-free transfer hydrogenation of ketone with FA as a hydrogen source in 1982.[17] Under neat conditions, formic acid and $RuCl_2(PPh_3)_3$ were mixed at 125 °C for three hours. The yield of alcohol was 84% using acetophenone as the model substrate. Later, the Shvo catalyst was reported for the transfer hydrogenation of ketones to alcohols without the use of a base, but the process was hampered by ester formation that could be avoided upon addition of a small amount of water and sodium formate.[18] Recently, Xu and Li reported *N*,*N*-chelated iridium chloride catalysts able to reduce a variety of ketones in water using a large excess of formic acid.[19] Few examples were also recently reported as part of scope studies. For instance, Ikariya reported an oxo-tethered ruthenium catalyst for the transfer hydrogenation of α-substituted acetophenones.[20] A modest conversion of 69% was obtained with a 1 mol% catalyst loading at 60 °C for 4 h. Sawamura *et al.* reported the reduction of acetophenone in 83% yield using 1 mol% of $[IrCl(cod)]_2$, a phosphine ligand and 2 equiv. of formic acid at room temperature for 6 h in CPME.[21] In 2018, a Shvo-type molybdenum catalyst was used for the transfer hydrogenation of acetophenone but a low yield of 22% was obtained at 65 °C in 48 h with a catalyst loading of 10 mol%.[22]

Overall, the vast majority of catalysts able to reduce ketones under base-free (and additive-free) conditions are either air or moisture sensitive organometallic complexes requiring rigorous conditions of an inert atmosphere and dry solvents. Transition metal complexes supported by often expensive ligands such as pincer-type ligands have also been extensively used. Easily accessible and stable complexes are therefore desirable for the base-free reduction of ketone and, more generally, for any transition metal-based catalytic transformation.

Over the past few years, we have been interested in the synthesis and use of catalysts bearing dipyridylamine ligands (dpa),[23] in particular for hydrogen storage purposes using formic acid as a liquid organic hydrogen carrier.[24] Recently, we have reported enhanced performances with electron enriched iridium complexes thanks to the introduction of electron-donating groups at the pyridine rings (Fig. 1). Indeed, the catalyst **Ir3** bearing the ligand **L3** with two dimethylamino substituents led to improved performances as compared to **Ir1** and **Ir2** respectively bearing ligands **L1** and **L2**. The key role of the sulfate ligand was also clearly evidenced.[25] During the synthesis of **L3**, the bipyridine ligand **L4** was obtained as a by-product. Later, this ligand was conveniently prepared using a reported procedure.[26] Of note, the iridium complexes **Ir1**–**Ir4** are easily obtained in two steps and good yields (>95%) as air-stable yellow powders.

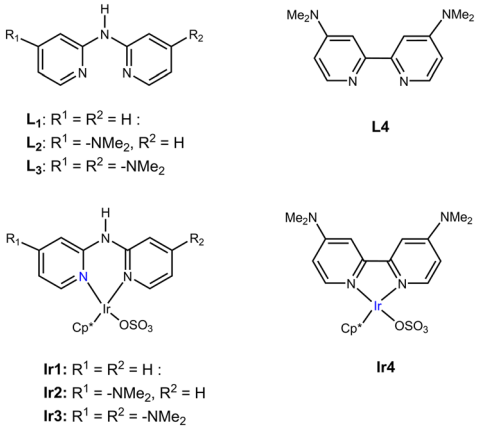


Fig. 1 Ligands and catalysts used in this study.

We present hereafter our work on the base-free reduction of ketones using catalysts **Ir1**–**Ir4** with a focus on the reduction of levulinic acid into γ-valerolactone.

Reduction of ketones

The four catalysts were evaluated in the aqueous phase hydrogenation of acetophenone under mild conditions of temperature (70 °C) and hydrogen pressure (10 bar). Due to the robustness of the catalysts, the reaction did not require the use of an inert atmosphere. As depicted in Table 1, all four catalysts were competent for the hydrogenation of acetophenone and the impact of increased electron donation evidenced in the dipyridylamine-based catalysts **Ir1**–**Ir3**. However, only the bipyridine **Ir4** catalyst reached nearly full conversion in 16 h (Table 1, entry 4) and full conversion could be reached upon increasing the temperature (Table 1, entry 5) or the pressure (Table 1, entry 6). Note that **Ir4** remains active at lower temperatures, but with lower substrate conversions (Table 1, entries 7 and 8). All reactions were conducted with a catalytic amount of formic acid. As shown in entries 7 and 8, lower conversions were achieved in the absence of formic acid. We believe that formic acid facilitates the formation of Ir–H species from iridium complexes. The formation of the same Ir–H species is most

Table 1 Hydrogenation of 1-acetophenone with dihydrogen[a]

Entry	Cat (mol%)	*P* H_2 (bar)	*T* (°C)	Conv.[b] (%)
1	**Ir1**	10	70	47
2	**Ir2**	10	70	61
3	**Ir3**	10	70	64
4	**Ir4**	10	70	95
5	**Ir4**	10	90	>99[c]
6	**Ir4**	20	70	>99[c]
7	**Ir4**	10	50	71 (38)[d]
8	**Ir4**	10	25	30 (16)[d]

[a] 1-Acetophenone (2 mmol), catalyst (0.1 mol%), H_2O (1 mL), formic acid (0.08 mol%), 16 h. [b] Determined by ^1H NMR. [c] 1-Acetophenone not detected. [d] Without formic acid.

certainly more difficult with dissolved dihydrogen, given the low solubility of dihydrogen in water.

The same four catalysts were then evaluated under transfer hydrogenation conditions using formic acid as a hydrogen donor.

One feature often neglected when using formic acid in catalytic reduction reactions is the real nature of the mechanism. Is it a true hydrogen transfer mechanism or does a fast formic acid dehydrogenation occur first? In the latter case, the reaction should be considered as a hydrogenation reaction with formic acid acting as a dihydrogen gas source. In 2017, we disclosed iridium–dipyridylamine catalysts capable of reducing levulinic acid into γ-valerolactone under base-free conditions. We demonstrated that the reaction proceeded by hydrogenation rather than transfer hydrogenation using a 2-compartment Schlenk tube, and the results of reactions conducted in a closed vessel *versus* open vessel.[27] In 2019, we have introduced one dimethylamino group on a dpa ligand which resulted in improved performances for the dehydrogenation of formic acid, including neat formic acid.[24a] In 2020, Kawanami and coworkers reported the utilisation of **Ir4**, bearing two –NMe_2 donor groups for the dehydrogenation of FA.[28]

Being a hydrogenation process, a closed experimental setup is necessary to ensure hydrogen pressure build-up. All reactions were thus conducted in identical and pressure resistant Ace®-tube[29] glass reactors to ensure reliability of the results (see the SI for safety recommendations).

As depicted in Table 2, **Ir4** was again the most efficient catalyst. However, higher reaction temperature was necessary to ensure high conversion. Having previously demonstrated the stability of our complexes under acidic conditions, it is likely that the lower performances are due to the lower hydrogen pressure achieved in Ace-tubes *vs.* the Parr reactors loaded at 10 bar of hydrogen. Despite these lower results, we believe that this process using formic acid as a hydrogen donor is of practical interest as it does not require expensive stainless-steel reactors and most of all it does not require the storage and handling of high-pressure hydrogen cylinders and valves.

Having optimised both protocols with **Ir4**, we have extended the scope of the reaction to other ketone derivatives with various steric and electronic properties. Hydrogenation with molecular hydrogen and formic acid as a hydrogen donor were studied and some limitations were identified (Fig. 2). The introduction of a methyl-substituent at the *ortho*-position did not hamper significantly the reaction providing **2** in 94% conversion. However, when the steric hindrance was increased, the efficiency of the reaction dropped significantly as demonstrated with compounds **5** and **7**. The very hindered alcohol **3** could not be obtained which is a limitation also reported in other reports or just not investigated. Steric hindrance also made camphor and menthone reluctant to hydrogenation (**21** and **22**) while the less hindered cyclohexanone was almost quantitatively converted to cyclohexanol **18**. The reaction tolerated well electron withdrawing groups leading to compounds **8**, **9**, **10** and **17** in good yields. It should however be noticed that under hydrogenation conditions, the bromo derivative led to a low conversion under hydrogenation conditions when using formic acid as a hydrogen source leading to 85% conversion.[30] The introduction of an electron donating group led to high conversion of the ketone reagents, but a selectivity issue arose as ether formation was observed up to 19% for **12′**. This type of etherification is not unknown and

Table 2 Hydrogenation of 1-acetophenone with formic acid as a hydrogen donor[a]

Entry	Cat (mol%)	t (h)	T (°C)	Conv.[b] (%)
1	**Ir2**	16	100	59
2	**Ir3**	16	100	67
3	**Ir4**	16	100	86
4	**Ir4**	24	100	93
5	**Ir4**	24	90	64

[a] 1-Acetophenone (2 mmol), catalyst (0.1 mol%), H_2O (1 mL), formic acid (4 mmol, 2 equiv.), 16 h. [b] Determined by ^{1}H NMR.

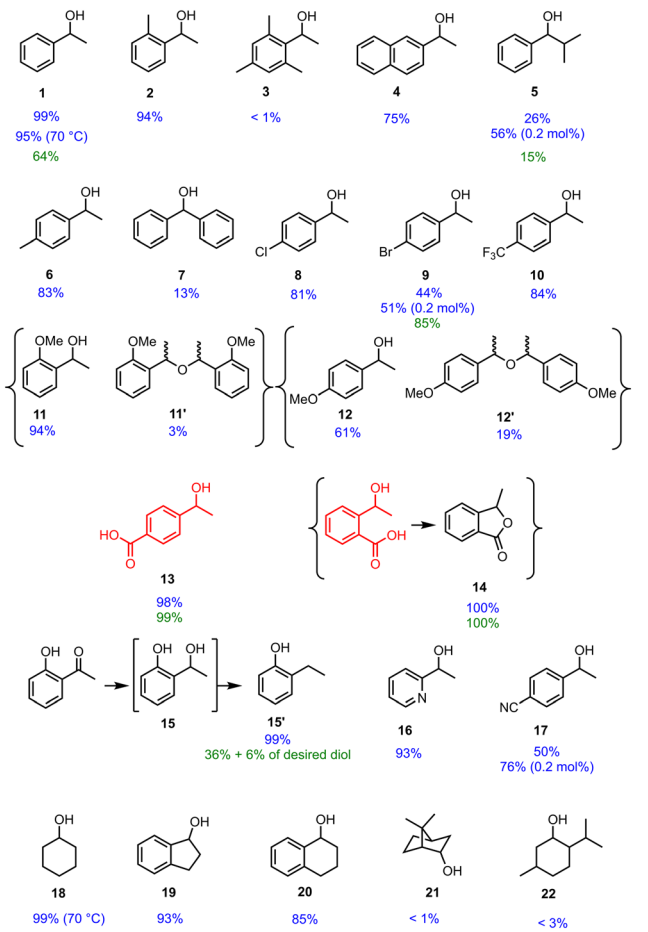


Fig. 2 Scope of reagents with **Ir4** (0.1 mol%) in water at 90 °C for 16 h. Conversion (%); blue = 10 bar H_2 and 0.08 mol% formic acid; green = 2 equiv. formic acid.

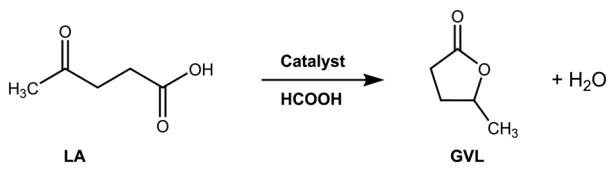
was previously reported by Andersson[12] (in dichloromethane) or Albrecht[31] (in toluene) and corresponds formally to an acid-promoted dehydration process.

We then turned our attention to base-sensitive reagents featuring acidic protons to highlight the interests of base-free conditions. The two (–CO_2H) substituted acetophenone derivatives were transformed with very high conversion in the desired product **13** for the *para*-substituted reagent and in the lactone **14** due to intramolecular esterification. Although it is not possible to have an exhaustive view of the very many reports on the base-assisted transition metal-catalysed reduction of ketones, we could not find this type of reagent into the substrate scope of the numerous articles surveyed. These compounds could only be found in recent articles on the base-free reduction of ketones and aldehydes.[19] Surprisingly, 2′-hydroxyacetophenone led to the deoxygenized compound **15′**. This type of reaction is not common and was only reported in a few articles on the deoxygenation of polyols.[32] We can therefore postulate that the diol **15** is first generated before deoxygenation occurs.

Reduction of levulinic acid

Levulinic acid (LA) is one of the biosourced platform chemicals from which a number of important raw materials for the chemical industry can be sourced.[33] γ-Valerolactone (GVL) is one of those compounds with numerous application domains. The synthesis of GVL has recently attracted a lot of attention in chemical research in particular in heterogeneous[34] and homogeneous catalysis.[35] In 2017, we reported our first results on the reduction of LA into GVL using ruthenium and iridium dipyridylamine catalysts and reported the highest TON at that time (174 000) employing an iridium catalyst.[27] We have pursued our effort to improve this transformation using catalysts with enhanced performances reported herein (Scheme 1). We selected a hydrogenation process using formic acid as a hydrogen source for its experimental practicability and easy implementation in any laboratory without the need for expensive high-pressure reactors and hydrogen storage facilities. Neat conditions were also selected as we previously showed that an Ir-dpa catalyst can almost equally perform in aqueous phase and under neat conditions. Furthermore, Ir-dpa catalysts also tolerate high formic acid concentrations.[24a]

The iridium dipyridylamine (dpa) catalysts were first evaluated, evidencing the beneficial impact resulting from the introduction of the dimethylamino-group on the dpa-ligand in **Ir3**. This catalyst was still active at 50 °C but with a lower rate (Table 3, entry 5). Conversely, the iridium-bpy catalyst **Ir4** was very active at nearly room temperature, remarkably providing full conversion of LA at 40 °C in 16 h and at 30 °C in 64 h (Table 3, entries 7 and 8). The catalyst loading could be further reduced to 0.01 mol%, still allowing full conversion at 90 °C in 16 h (Table 3, entry 9).



Scheme 1 Reduction of levulinic acid into GVL.

Table 3 Hydrogenation of levulinic acid with formic acid as a hydrogen donor under neat conditions[a]

Entry	Cat (mol%)	t (h)	T (°C)	Conv.[b] (%)	TON[d]
1	**Ir1** (0.1 mol%)	16	110	73	730
2	**Ir2** (0.1 mol%)	16	110	72	720
3	**Ir3** (0.1 mol%)	16	110	97	970
4	**Ir3** (0.1 mol%)	16	90	81	810
5	**Ir3** (0.1 mol%)	16	50	34	340
7	**Ir4** (0.1 mol%)	16	40	100[c]	100
8	**Ir4** (0.1 mol%)	64	30	100[c]	1000
9	**Ir4** (0.01 mol%)	16	90	100[c]	10 000

[a] LA (0.232 g, 2 mmol), FA (0.184 g, 4 mmol). [b] Determined by ^{1}H NMR. [c] LA not detected by ^{1}H NMR. [d] Mol of LA converted per mol of the catalyst.

These results are quite similar to those reported by Fu in 2013 with an iridium catalyst supported by a bpy-OMe ligand under diluted conditions (1 M aqueous solution of LA).[36] The introduction of a dimethylamino-substituent on the bpy core thus leads to great improvement, since **Ir4** displays similar efficiency to Fu's catalyst, but under neat conditions.

Reaction mechanism

The reaction mechanism comprises two essential steps, the first one leading to the formation of the Ir–H species **B** (Fig. 3). When formic acid is used for reduction reactions, the mechanism is in general considered as a transfer hydrogenation reaction. However, we and others have demonstrated that catalysts such as **Ir1**–**Ir4** are very efficient for the fast dehydrogenation of formic acid (Fig. 3, I + cycle II).[24a,25,28] In fact, when reactions are conducted in an open vessel, yields drop considerably to 25–30%. The reversibility of FA dehydrogenation could ensure

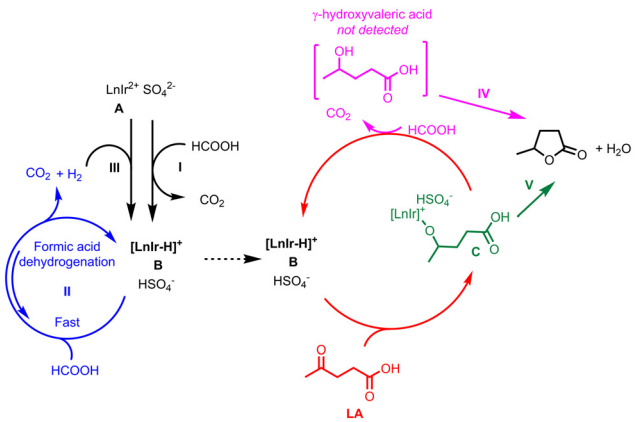


Fig. 3 Postulated mechanism for the formation of GVL.

the availability of FA once the equilibrium was reached in a closed vessel (cycle **II**, Fig. 3). However, our experience shows that this type of iridium catalyst is poorly efficient in the hydrogenation of CO_2 so we do not consider this path as a realistic one. Alternatively, the iridium precursor **A** was found to be competent for the activation of dihydrogen (Fig. 3, **III**), as demonstrated earlier in this manuscript. Under base-free conditions, we postulated in our first report the involvement of the SO_4^{2-} anion in the deprotonation of FA.[27] This was later confirmed by theoretical calculation from Li using a bpy-iridium model[37] and recently by us with a dpa-iridium complex.[25] The second part of the mechanism deals with the hydride transfer, which could occur by insertion of the carbonyl functional group in the Ir–H species. If the migratory insertion of the carbonyl bond into the M–H is a well-known process, the terminal formation of GVL is not well documented. Indeed, the vast majority of reports on GVL formation by reduction of levulinic acid state the release of γ-hydroxyvaleric acid that undergoes intramolecular esterification (Fig. 3, pathway **IV**). However, the identification of γ-hydroxyvaleric acid in the reaction mixture has never been clearly reported even in studies with *in situ* monitoring of reaction progress by ^{1}H NMR and FTIR.[38] This matter of fact prompted us to postulate in 2017 a metal-assisted cyclisation process leading to GVL.[27] This alternative mechanism was further demonstrated to be feasible by DFT studies using dihydrogen.[37] Having again been unable to detect the formation of γ-hydroxyvaleric acid by ^{1}H NMR at different conversions (30, 60, and 120 min), we have performed DFT studies to identify a possible reaction mechanism (Fig. 3, pathway **V**).

DFT study

We carried out DFT calculations using the M06L[39] functional, the Stevens/Basch/Krauss relativistic effective core potential triple-split basis (CEP-121G)[40] for Ir, and the 6-31G(d,p)[41] basis set for other atoms. Single point energy calculations were performed with a larger def2TZVP[42] basis set using an SMD solvent model with water (see computational details in the SI).

Considering that the mechanism was already investigated by Li and coworkers[37] with a similar complex under hydrogenation conditions, we have considered the first step only to identify possible pathways involving formic acid for the generation of catalytically relevant Ir-hydride species **A** (Fig. 4). Starting from the most likely precursor, the iridium-aquo **Int1**,[43] we have identified the formic acid coordinated **Int2** of similar energy. From this intermediate, we could localise direct hydride transfer **TS1** with an accessible energy barrier of 12 kcal mol^{-1} in which the SO_4^{2-} anion acts as a base, abstracting a proton as reported in our previous studies.[27] **TS1** evolves toward the stable Ir–H species **A** with the release of CO_2 (Fig. 4, blue pathway). We have also considered a formate pathway although no base was used as a co-catalyst in the reduction reaction (Fig. 4, pink pathway).

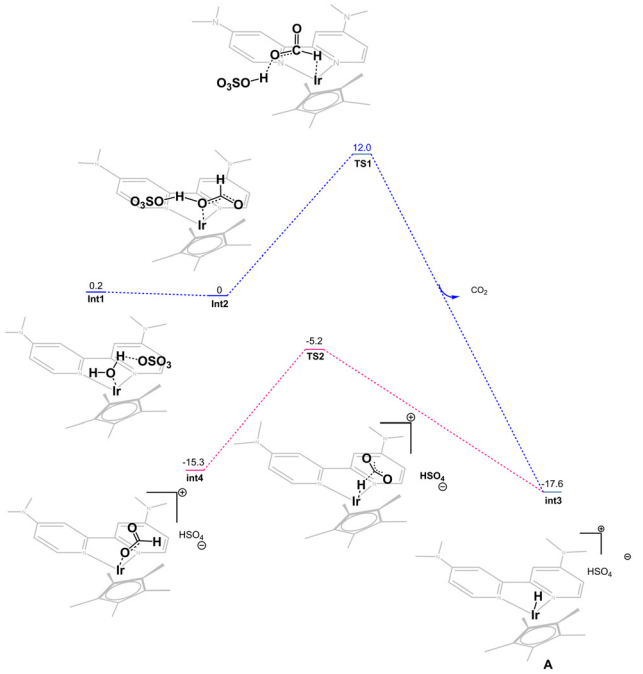


Fig. 4 DFT calculated energy profile for the formation of the Ir-hydride species **A**. Relative free energy (kcal mol^{-1}) (M06L, def2TZVP, SMD solvent model with water).

Indeed, even though formic acid is a weak acid, furthermore used neat in the absence of water (except that from supplied formic acid and levulinic acid) and water produced by the reaction, the amount of formate ions resulting from dissociation should not be neglected. An approximate calculation by two different methods revealed an amount of formate ions of 0.016–0.022 mmol in the reaction mixture, and thus about 8–11 times higher than the 0.002 mmol of

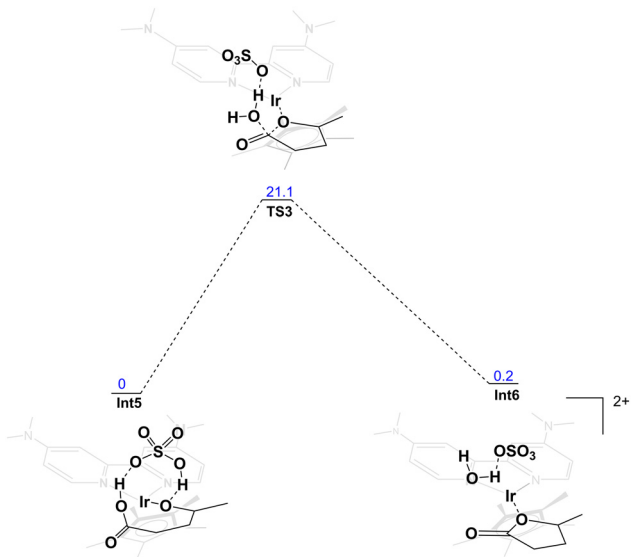


Fig. 5 Metal-assisted GVL formation. Relative free energy (kcal mol^{-1}) (M06L, def2TZVP, SMD solvent model with water).

the catalyst (see the SI). The formate pathway was thus considered and the iridium-formate **Int4** found lower in energy lying 15.3 kcal below **Int2**. However, the energy barrier to generate the Ir-hydride **A** (**Int3**) through **TS2** was very similar (10.1 kcal mol^{-1}). This confirms that a formate mechanism should not be discarded when working at low catalyst loading, even though the reaction is conducted in the absence of a base.

We then considered the metal-assisted generation of GVL (Fig. 5), because, as explained above, γ-hydroxyvaleric acid, the presumed precursor of GVL by intramolecular esterification, was not detected upon monitoring the reaction by ^1H NMR. As computed by Li[37] with a related complex bearing a 4,4′-dimethoxy-2,2′-bipyridine ligand, we have identified **Int5** as a possible intermediate arising from a hydride transfer to the carbonyl group. This step was fully documented and reported by Li. We have computed the evolution of **Int5** and found that it could release GVL *via* **TS3** with an accessible activation energy of 21.1 kcal mol^{-1}, and thus in agreement with Li's findings who reported an activation energy of 26.8 kcal mol^{-1} using identical computation methods and parameters. This intramolecular cyclisation formally corresponds to a nucleophilic attack of the alkoxylate on the activated carbonyl moiety assisted by HSO_4^-.

Conclusions

In this article, we have demonstrated the ability of a series of iridium-based catalysts to reduce various ketones in the absence of any additives, particularly bases. Of note, the most active catalyst **Ir4**, bearing an electron-rich bipyridine ligand, is active at 25 °C under hydrogenation conditions. This catalyst is also very active when formic acid is used as a dihydrogen source in a closed vessel. In this case, a higher temperature is necessary to ensure high conversion. A broad scope of substrates has been investigated, highlighting their excellent performances along with some limitations. The absence of any base has enabled the use of ketones substituted with a carboxylic acid functionality, which are not covered by conventional catalysts operating under basic conditions. We have extended the scope to levulinic acid and its reduction to γ-valerolactone (GVL). **Ir4** was again found to be very active affording full conversion of levulinic acid at temperature as low as 30 °C using formic acid as a dihydrogen source. DFT calculations were conducted to propose a reaction mechanism. In particular, the formation of the key Ir–H intermediate was closely investigated. The involvement of the SO_4 dianion acting as a base in the reaction mechanism was evidenced. Besides the very good catalytic performances achieved with low catalyst loadings (0.01 mol% to 0.1 mol%), the contribution to sustainable chemistry should also be highlighted since the reaction media used were either aqueous or solvent-free.

Author contributions

L. Guo and Z. Li: investigation, methodology, and formal analysis. R. Marchal and B. Le Guennic: validation. C. Fischmeister: conceptualisation, formal analysis, project administration, resources, supervision, validation, and manuscript writing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Data include the NMR spectra for the synthesized compounds and coordinates for DFT calculations.

Supplementary information is available. See DOI: https://doi.org/10.1039/d6cy00010j

Notes and references

1 (*a*) M. Kitamura, M. Tokunaga and R. Noyori, *J. Am. Chem. Soc.*, 1995, **117**, 2931–2932; (*b*) N. Uematsu, A. Fujii, S. Hashiguchi, T. Ikariya and R. Noyori, *J. Am. Chem. Soc.*, 1996, **118**, 4916–4917; (*c*) R. Noyori, *Angew. Chem., Int. Ed.*, 2002, **41**, 2008–2022.
2 (*a*) R. Noyori and T. Ohkuma, *Angew. Chem., Int. Ed.*, 2001, **40**, 40–73; (*b*) D. Wang and D. Astruc, *Chem. Rev.*, 2015, **115**, 6621–6686.
3 (*a*) A. Ouali, J.-P. Majoral, A.-M. Caminade and M. Taillefer, *ChemCatChem*, 2009, **1**, 504–509; (*b*) M. D. Le Page and B. R. James, *Chem. Commun.*, 2000, 1647–1678; (*c*) M. C. Carrion, F. Sepulveda, F. A. Jalon and B. R. Manzano, *Organometallics*, 2009, **28**, 3822–3833.
4 Y. Blum, D. Czarkle, Y. Rahamim and Y. Shvo, *Organometallics*, 1985, **4**, 1459–1461.
5 T. Ohkuma, N. Utsumi, K. Tsutsumi, K. Murata, C. Sandoval and R. Noyori, *J. Am. Chem. Soc.*, 2006, **128**, 8724–8725.
6 T. Ohkuma, K. Tsutsumi, N. Utsumi, N. Arai, R. Noyori and K. Murata, *Org. Lett.*, 2007, **9**, 255–257.
7 R. Langer, M. A. Iron, L. Konstantinovski, Y. Diskin-Posner, G. Leitus, Y. Ben-David and D. Milstein, *Chem. – Eur. J.*, 2012, **18**, 7196.
8 G. Zhang, K. V. Vasuvedan, B. L. Scott and S. Hanson, *J. Am. Chem. Soc.*, 2013, **135**, 8668–8681.
9 F. Jiang, K. Yuan, M. Achard and C. Bruneau, *Chem. – Eur. J.*, 2013, **19**, 10343–10352.
10 Z.-J. Yao, J.-W. Zhu, N. Lin, X.-C. Qiao and W. Deng, *Dalton Trans.*, 2019, **48**, 7158–7166.
11 R. Wang, J. Qi, Y. Yue, Z. Lian, H. Xiao, S. Zhuo and L. Xing, *Tetrahedron*, 2019, **75**, 130463.
12 X. Quan, S. Kerdphon, B. B. C. Peters, J. Rujirawanich, S. Krajanggsri, J. Jongcharoenkamol and P. G. Andersson, *Chem. – Eur. J.*, 2020, **26**, 13311–13316.

13 S. Weber, J. Brünig, L. F. Veiros and K. Kirchner, *Organometallics*, 2021, **40**, 1388–1394.
14 (*a*) M. Bianchi, U. Matteoli, G. Menchi, P. Frediani, S. Pratesi, F. Piacenti and C. Botteghi, *J. Organomet. Chem.*, 1980, **198**, 73–80; (*b*) Y. Lin and Y. Zhou, *J. Organomet. Chem.*, 1990, **381**, 135–138; (*c*) E. Mizushima, M. Yamagushi and T. Yamagishi, *Chem. Lett.*, 1997, **26**, 237–238; (*d*) E. Mizushima, M. Yamagushi and T. Yamagishi, *J. Mol. Catal. A: Chem.*, 1999, **148**, 69–75, 1997, 26, 237–238; (*e*) C. Bianchini, E. Farnetti, M. Graziani, M. Peruzzini and A. Polo, *Organometallics*, 1993, **12**, 3753–3761.
15 (*a*) Z.-R. Dong, Y.-Y. Li, J.-S. Chen, B.-Z. Li, Y. Xing and J.-X. Gao, *Org. Lett.*, 2005, **7**, 1043–1045; (*b*) Z. E. Clarke, P. T. Maragh, T. P. Dasgupta, D. G. Gusev, A. J. Lough and K. Abdur-Rashid, *Organometallics*, 2006, **25**, 4113–4117.
16 (*a*) R. Corberán and E. Peris, *Organometallics*, 2008, **27**, 1954–1958; (*b*) A. G. Elliott, A. G. Green and P. L. Diaconescu, *Dalton Trans.*, 2012, **41**, 7852–7854; (*c*) A. Ruff, C. Kirby, B. C. Chan and A. R. O'Connor, *Organometallics*, 2016, **35**, 327–335; (*d*) M. G. Sommer, S. Marinova, M. J. Krafft, D. Urankar, D. Schweinfurth, M. Bubrin, J. Košmrlj and B. Sarkar, *Organometallics*, 2016, **35**, 2840–2849; (*e*) M. Navarro, C. A. Smith and M. Albrecht, *Inorg. Chem.*, 2017, **56**, 11688–11701; (*f*) R. A. Farrar-Tobar, Z. Wei, H. Jiao, S. Hinze and J. G. de Vries, *Chem. – Eur. J.*, 2018, **24**, 2725–2734; (*g*) P. Dubey, S. Gupta and A. K. Singh, *Organometallics*, 2019, **38**, 944–961; (*h*) A. M. Kalsin, T. A. Peganova, I. S. Snopalnikova, I. V. Fedyanin, N. V. Belkova, E. Deydier and R. Poli, *Dalton Trans.*, 2020, **49**, 1473–1484.
17 Y. Watanabe, T. Ohta and Y. Tsuji, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2441–2445.
18 N. Menashe, E. Salant and Y. Shvo, *J. Organomet. Chem.*, 1996, **514**, 97–102.
19 (*a*) J.-T. Liu, S. Yang, W. Tang, Z. Yang and J. Xu, *Green Chem.*, 2018, **20**, 2118–2124; (*b*) Z. Yang, W. Cheng and Z. Li, *Catal. Commun.*, 2018, **117**, 38–42.
20 Y. Yuki, T. Touge, H. Nara, K. Matsumura, M. Fujiwhara, Y. Kayaki and T. Ikariya, *Adv. Synth. Catal.*, 2018, **360**, 568–574.
21 H. Murayama, Y. Heike, K. Higashida, Y. Shimizu, N. Yodsin, Y. Wongnongwa, S. Jungsuttiwong, S. Mori and M. Sawamura, *Adv. Synth. Catal.*, 2020, **362**, 1–8.
22 W. Wu, T. Seki, K. L. Walker and R. M. Waymouth, *Organometallics*, 2018, **37**, 1428–1431.
23 (*a*) S. Wang, C. Bruneau, J.-L. Renaud, S. Gaillard and C. Fischmeister, *Dalton Trans.*, 2019, **48**, 11599–11622; (*b*) S. Wang, H. Huang, C. Bruneau and C. Fischmeister, *ChemSusChem*, 2019, **12**, 2350–2354; (*c*) S. Wang, H. Huang, C. Bruneau and C. Fischmeister, *ChemSusChem*, 2017, **10**, 4150–4154; (*d*) S. Wang, V. Dorcet, T. Roisnel, C. Bruneau and C. Fischmeister, *Organometallics*, 2017, **36**, 708–713.
24 (*a*) S. Wang, H. Huang, T. Roisnel, C. Bruneau and C. Fischmeister, *ChemSusChem*, 2019, **12**, 179–184; (*b*) R. Verron, E. Puig, P. Sutra, A. Igau and C. Fischmeister, *ACS Catal.*, 2023, **13**, 5787–5794.
25 L. Guo, Z. Li, M. Cordier, R. Marchal, B. Le Guennic and C. Fischmeister, *ACS Catal.*, 2023, **13**, 13626–13637.
26 For an alternative synthesis of L4, see: G.-J. ten Brink, I. W. C. E. Arends, M. Hoogenraad, G. Verspui and R. Sheldon, *Adv. Synth. Catal.*, 2003, **345**, 497–505.
27 S. Wang, H. Huang, V. Dorcet, T. Roisnel, C. Bruneau and C. Fischmeister, *Organometallics*, 2017, **36**, 3151–3162.
28 H. Kawanami, M. Iguchi and Y. Himeda, *Inorg. Chem.*, 2020, **59**, 4191–4199.
29 Ace tubes are commercially available glass reactors with a pressure rating of 150 psig (10 bar) at 120 °C, http://www.aceglass.com.
30 Unreacted *p*-bromo-acetophenone was recovered. A debrominated product was not observed.
31 I. D. Alshakova and M. Albrecht, *ACS Catal.*, 2021, **11**(15), 8999–9007.
32 (*a*) D. B. Lao, A. C. E. Owens, D. M. Heinekey and K. I. Goldberg, *ACS Catal.*, 2013, **3**, 2391–2396; (*b*) M. Schlaf, P. Ghosh, P. J. Fagan, E. Hauptman and R. M. Bullock, *Angew. Chem., Int. Ed.*, 2001, **40**, 3887–3890; (*c*) Z. Yang, X. Zhu, S. Yang, W. Cheng, X. Zhang and Z. Yang, *Adv. Synth. Catal.*, 2020, **362**, 5496–5505; (*d*) S. Yang, W. Tang, Z. Yang and J. Xu, *ACS Catal.*, 2018, **8**, 9320–9326.
33 (*a*) A. Victor, P. Sharma, I. N. Pulidindi and A. Gedanken, *Catalysts*, 2022, **12**, 909; (*b*) F. D. Pileidis and M.-M. Titirici, *ChemSusChem*, 2016, **9**, 562–582.
34 (*a*) R. Xu, K. Liu, H. Du, H. Liu, X. Cao, X. Zhao, G. Qu, X. Li, B. Li and C. Si, *ChemSusChem*, 2020, **13**, 1–17; (*b*) W. R. H. Wright and R. Palkovits, *ChemSusChem*, 2012, **5**, 1657–1667.
35 (*a*) F. Joo, Z. Toth and T. Beck, *Inorg. Chim. Acta*, 1977, **25**, L61–L62; (*b*) U. Omoruyi, S. Page, J. Hallett and P. W. Miller, *ChemSusChem*, 2016, **9**, 2037–2047.
36 J. Deng, Y. Wang, T. Pan, Q. Xu, Q.-X. Guo and Y. Fu, *ChemSusChem*, 2013, **6**, 1163–1167.
37 J. Li, Y. Yang, H. Di and J. Wang, *J. Org. Chem.*, 2021, **86**, 674–682.
38 J. M. Tukacs, D. Király, A. Strádi, G. Novodarszki, Z. Eke, G. Dibó, T. Kégl and L. T. Mika, *Green Chem.*, 2012, **14**, 2057–2064.
39 Y. Zhao and D. G. Truhlar, *J. Chem. Phys.*, 2006, **125**, 194101.
40 (*a*) W. J. Stevens, M. Krauss, H. Basch and P. G. Jasien, *Can. J. Chem.*, 1992, **70**, 612–630; (*b*) T. R. Cundari and W. J. J. Stevens, *Chem. Phys.*, 1993, **98**, 5555–5565.
41 W. J. Hehre, K. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261.
42 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
43 Although the reaction was carried out in the absence of solvent (water), water can be brought in the reaction by formic acid and levulinic acid that are used as received. Water is also released upon formation of GVL.