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Ruthenium and Iridium Dipyridylamine Catalysts for the Efficient Synthesis of γ -Valerolactone by Transfer Hydrogenation of Levulinic Acid.

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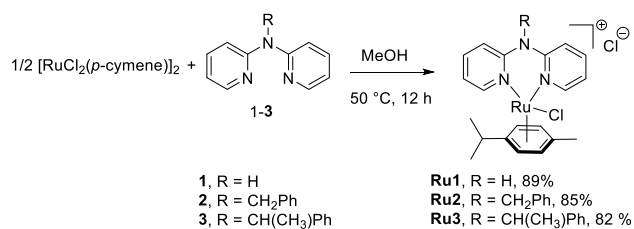
Supporting Information Placeholder

ABSTRACT: The selective and efficient transfer hydrogenation of levulinic acid into γ -valerolactone was performed with new ruthenium and iridium catalysts bearing dipyridylamine (dpa) ligands. Reactions were performed in the presence of formic acid and triethylamine using catalyst loading as low as 0.05 mol% with a ruthenium complex (TON 1980). Recyclability of a ruthenium catalyst was demonstrated by running 6 consecutive reactions in almost quantitative yields.

The development of efficient and environmentally friendly chemical processes is a crucial challenge for the transformation of bio-sourced compounds meant for replacing fossil resources in the near future.¹ In this context, catalysis will undoubtedly be a key actor to address the growing demand of bio-fuels and bio-sourced chemicals.² Carbohydrates represent by far the highest volume of accessible biomass. They have thus received a great deal of attention as source of bio-fuels and platform chemicals from which a huge number of valuable compounds and synthetic intermediates are accessible.³ Back in 2004, the DOE listed a series of 12 building blocks derived from carbohydrates that can be further converted to a number of high-value bio-based chemicals or materials.⁴ Recently, this list was revisited and extended to 14 platform chemicals.⁵ Levulinic acid (LA) is considered as one of the most interesting compound of these platform chemical as it offers 2 reactive functional groups and it is available at low cost as a cellulose waste. Among its various uses, LA is a platform chemical for the production a fuel additives and it can also be transformed into several high-value compounds such as 2-methyltetrahydrofuran or γ -valerolactone.^{6,7} Several homogeneous and heterogeneous catalysts have been reported for the hydrogenation of LA while fewer reports deal with transfer hydrogenation of LA.^{7b} In homogeneous catalysis, only few studies have been reported with Ru,⁸ Ir,⁹ Pd¹⁰ and Fe.¹¹ To date, the best results were reported in 2014 by Horvath using the bifunctional Shvo catalyst.^{8c} Due to the specificity of this catalyst, TON as high as 2400 were obtained at 100 °C without additional base. Iridium complexes bearing bis-pyridine ligand also demonstrated interesting results and potential in the transfer hydrogenation of LA.⁹ In a general manner, *N,N*-Chelating ligands such as bis-pyridines, bis-imines or bis-oxazolines play a pivotal role in organometallic chemistry for

the synthesis of compounds with luminescent or catalytic properties. Despite the structural diversity now easily accessible by catalytic amination reactions,¹² dipyridylamine (dpa) has received little attention as ligand in homogeneous catalysis¹³ or luminescent materials.¹⁴ In 2010, we have reported the aqueous phase transfer hydrogenation of ketones by ruthenium(dpa) complexes demonstrating the potential of dpa ligands in such transformations.¹⁵ Herein we present the synthesis, characterization and catalytic activity in the transfer hydrogenation of LA of a series of new ruthenium and iridium dpa complexes.

Previous studies involving ruthenium catalysts have shown the superiority of *p*-cymene containing complexes in transfer hydrogenation of ketones.¹⁵ With this in mind, we have prepared two new arene-ruthenium complexes **Ru2,3** along with the known **Ru1**¹⁵ complex in order to evaluate the influence of the steric bulk at by the bridging nitrogen atom. Furthermore, substitution of the *N-H* by a *N-R* bridge should also provide some information on the potential involvement of the acidic *N-H* in an outer-sphere mechanism. Complexes **Ru1-3** were obtained in good yields from [RuCl₂(*p*-cymene)]₂ and the corresponding dpa-ligand (Scheme 1, see SI for ligand synthesis).



Scheme 1. Synthesis of ruthenium complexes

All three complexes were characterized by X-ray analyses. The molecular structures show in all cases a pseudotetrahedral arrangement of the ligands around the ruthenium atom. However, some important variations are observed between the secondary amine bridged **Ru1** and the two tertiary-amine bridged **Ru2** and **Ru3**. As depicted in table 1, the dpa ligand is almost planar in **Ru1** with an angle of 150.78° between the mean-plane containing the pyridine rings and the bridging nitrogen atom whereas this angle was only 127.28° and 125.39° in **Ru2** and **Ru3** respectively (Table 1 & Figure 1). Relative steric interactions between the *p*-cymene and *N*-substituted dpa ligand results in distortion of the dpa ligand hence impacting its coordination properties.

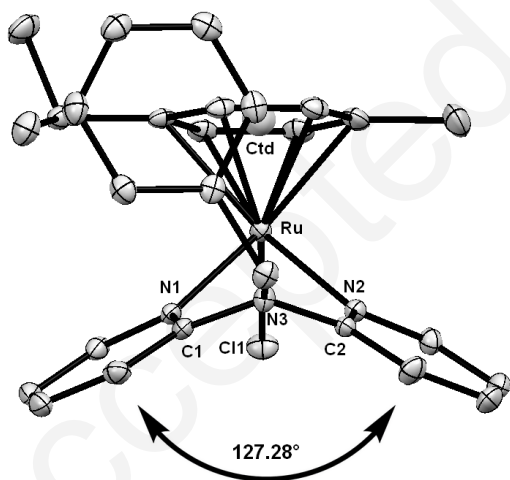
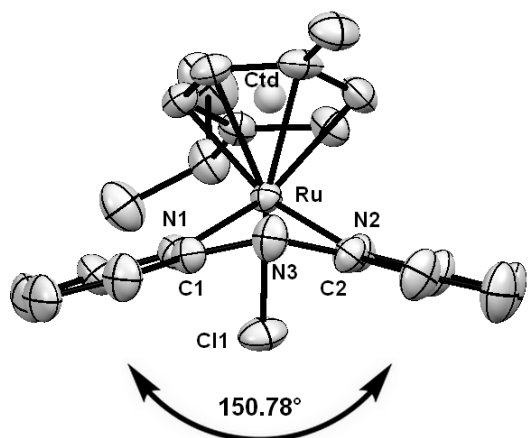


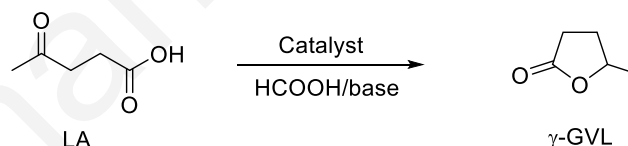
Figure 1 Molecular structures of **Ru1** (top) and **Ru2** (bottom). Ellipsoid shown at 50% probability. H, Cl counter-anion omitted for clarity.

Table 1 Structural data for **Ru1-3**^a

Entry		Ru-1	Ru-2	Ru-3
1	Ru-N1	2.103	2.102	2.104
2	Ru-N2	2.091	2.109	2.111
3	Ru-Cl	2.392	2.406	2.394
4	N3-C1	1.383	1.409	1.417
5	N3-C2	1.378	1.408	1.412
6	Ru-Ctd ^b	1.681	1.681	1.682
7	N1RuN2	85.05	80.98	83.03
8	C1N3C2	127.55	117.84	115.28
9	PyN3Py ^c	150.78	127.28	125.39

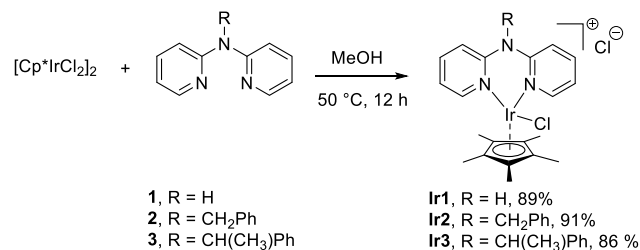
^abond lengths (Å), angles (°). ^bCtd = *p*-cymene centroid. ^cmean plane calculated from pyridine rings and N3

The three complexes were evaluated in the solvent free transfer hydrogenation of levulinic acid (Scheme 2). An initial catalyst free blank test realized with 2 equiv. of formic acid (FA) and 1 equiv. of Et₃N did not show any conversion of LA. A preliminary screening of various parameters was first performed with **Ru1** and extended to **Ru2** and **Ru3** (Table 2).



Scheme 2. Transfer hydrogenation of levulinic acid (LA)

This screening revealed the necessity to run the reaction at 150 °C in the presence of a base. Several bases were evaluated (see ESI) from which triethylamine provided the best results as often observed in transfer hydrogenation employing FA/Et₃N. In all cases, reactions were clean and selective producing only γ -GVL. Of note the catalyst **Ru3** with the bulkiest dpa ligand delivered the best performances with a yield of 99% obtained at low 0.05 mol% catalyst loading (Table 2, entry 9). This result corresponds to a TON of 1980, close to the highest TON reported so far by Horváth (TON 2400)^{8c} and higher than TONs reported in other transfer hydrogenation of LA. Further decrease of the catalyst loading lead to modest yield in 16 h. However, prolonged heating provided higher yield and a TON of 2766 hence demonstrating the high stability of the catalyst under these experimental conditions (Table 2, entries 10, 11). The transformation could also be performed at lower temperature but higher amounts of formic acid and base were necessary to maintain high yields of γ -GVL (Table 2, entries 8 & 12, 13).



Scheme 3 Synthesis of Iridium complexes

Table 2 Transfer hydrogenation with ruthenium catalysts^a

Entry	Cat (mol%)	T (°C)	FA (equiv.)	Et ₃ N (equiv)	Yield ^b (%)
1	Ru1 (0.1)	150	2	1.5	75
2	Ru1 (0.1)	150	2	1	99 (95)
3 ^c	Ru1 (0.1)	150	2	0.5	82
4	Ru1 (0.1)	150	2	0	6
5	Ru1 (0.1)	150	1.5	1	72
6	Ru1 (0.1)	120	2	1	23
7	Ru2 (0.1)	150	2	1	87
8	Ru3 (0.1)	150	2	1	100
9	Ru3 (0.05)	150	2	1	99
10	Ru3 (0.03)	150	2	1	55
11 ^d	Ru3 (0.03)	150	2	1	83
12	Ru3 (0.1)	120	2	1	52
13	Ru3 (0.1)	120	4	2	99 (98)

^a LA (0.23 g, 2 mmol), Et₃N (equiv. as indicated), FA (equiv. as indicated), 16 h. ^bdetermined by ¹H NMR (isolated yields). ^ccondition used for base screening, see ESI. ^d48 h

Following these very promising results obtained with ruthenium complexes and considering recent reports on iridium-bispyridine catalysts⁹ we have prepared and studied a second series of dpa-iridium complexes. The known **Ir1**¹⁶ and the new **Ir2,3** were prepared applying the same procedure than that used for the syntheses of the ruthenium complexes (Scheme 3).

The three iridium complexes were obtained in very good yields and characterized by X-ray diffraction. As reported in Table 3, **Ir1** displayed structural data almost identical as to **Ru1** in particular an almost planar dpa ligand (Table 3, entry 9). Similarly, **Ir3** and **Ru3** shared common structural data such as bent dpa ligand (Table 3 entry 9 and Table 1 entry 9), respectively. The main difference between this two series of complexes was observed with **Ru2** and **Ir2**. Indeed, if **Ru2** displayed structural data close to **Ru3**, i.e. featuring a bent dpa (Table 1, entry 9), the structure of **Ir2** was close to that of **Ir1** containing a more planar dpa ligand (Table 3, entry 9). We assume that the conflicting steric pressure exerted by the two pyridine rings of dpa and the Cp* ligand on the *N*-substituent is at the origin of this structural difference. As shown in Figure 2, the benzyl substituent in **Ir2** is oriented toward the pyridine ring of the dpa ligand whereas it is oriented towards the *p*-cymene ligand in **Ru2** (Figure 1).

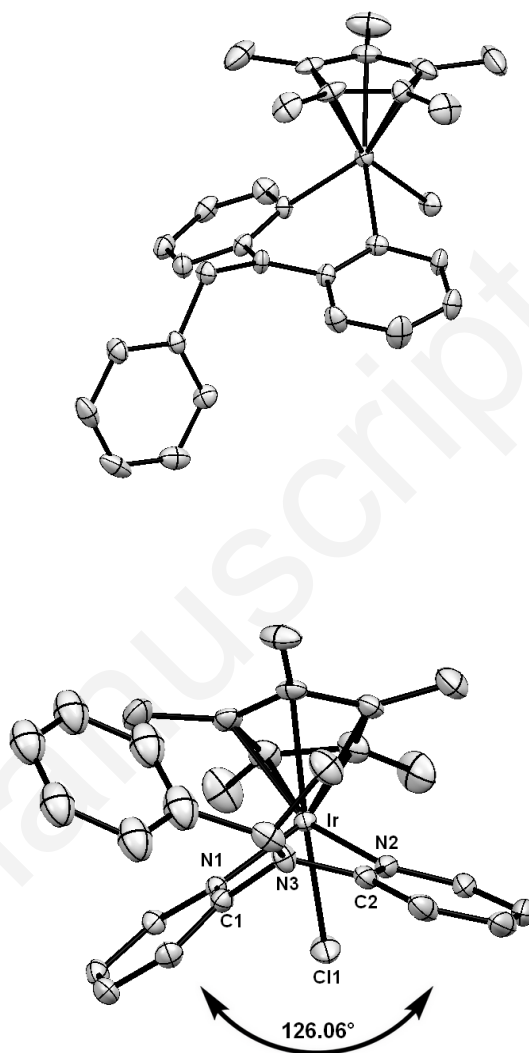


Figure 2 Molecular structures of **Ir2** (top) and **Ir3** (bottom). Ellipsoid shown at 50% probability. H, Cl counter-anion and solvent omitted for clarity.

Table 3 Structural data for Ir1-3^a

Entry		Ir1	Ir2	Ir3
1	Ir-N1	2.102	2.086	2.097
2	Ir-N2	2.094	2.107	2.098
3	Ir-Cl	2.388	2.413	2.405
4	N3-C1	1.373	1.405	1.412
5	N3-C2	1.375	1.411	1.414
6	Ir-Ctd ^b	1.778	1.780	1.780
7	N1IrN2	83.96	83.07	83.94
8	C1N3C2	127.90	125.10	115.55
9	PyN3Py ^c	153.55	151.19	126.06

^abond lengths (Å), angles (°). ^b Ctd = Cp* centroid. ^caverage plane calculated from pyridine rings and N3

The three iridium complexes **Ir1-3** were also evaluated in the solvent free transfer hydrogenation of levulinic acid to γ -valerolactone under similar conditions as those implemented with ruthenium complexes. A difference between ruthenium and iridium complexes was revealed by these results. Indeed, the more sterically congested **Ir3** containing a bent-dpa ligand was found to be the less efficient catalyst as opposed to the results obtained with ruthenium complexes where the sterically encumbered **Ru3** was indeed the most efficient one. Due to the lack of knowledge on the structure/coordination properties relationship in dipyriddyamine containing complexes, any interpretation of this observation would be highly uncertain. Another difference with ruthenium catalysts was revealed. Increasing temperature to 150 °C led to lower γ -GVL yields (Table 4, entries 1-5 for **Ir1**; 6-7 for **Ir2** and 8-9 for **Ir3**). This behaviour could result from a lower thermal stability of iridium complexes but it could also result from FA dehydrogenation occurring at higher temperature knowing that **Ir1** is a poor hydrogenation catalyst.¹⁷

Table 4 Transfer hydrogenation with iridium catalysts^a

Entry	Cat (mol%)	T (°C)	FA (equiv.)	Et ₃ N (equiv)	Yield ^b (%)
1	Ir1 (0.1)	150	2	1	50
2	Ir1 (0.1)	140	2	1	48
3	Ir1 (0.1)	130	2	1	59
4	Ir1 (0.1)	120	2	1	70 (68)
5	Ir1 (0.1)	110	2	1	66
6	Ir2 (0.1)	120	2	1	64 (63)
7	Ir2 (0.1)	150	2	1	33
8	Ir3 (0.1)	120	2	1	30
9	Ir3 (0.1)	150	2	1	22
10	Ir1 (0.1)	120	2	1.5	75
11	Ir1 (0.1)	120	3	1	72
12	Ir1 (0.1)	120	4	2	98 (95)
13	Ir1 (0.05)	120	4	2	80

^a LA (0.23 g, 2 mmol), Et₃N (equiv. as indicated), FA (equiv. as indicated), 16 h. ^bdetermined by ¹H NMR (isolated yield).

The viability of a catalytic system does not only rely on catalyst efficiency but also on its ability to be used in a continuous process or reused in batch experiments. To assess the potential of our new catalyst in this domain we have submitted **Ru3** to a series of catalytic runs.^{18, 19} After a first run performed under Table 1, entry 9 conditions (i.e. 0.05 mol% catalyst loading, 16 h), the crude reaction mixture was analyzed by ¹H NMR to confirm full conversion of levulinic acid. All volatile compounds were then distilled off and trapped in a cold bath. γ -GVL was then isolated by column chromatography on silica gel in almost quantitative yield. The remaining crude reaction mixture was then reloaded with levulinic acid, formic acid and triethylamine and a second run was performed yielding γ -GVL in 99% isolated yield. Up to 6 runs could then be performed without decrease of the isolated yields hence demonstrating the high sta-

bility and recyclability of the catalytic system (Figure 3). Similarly, **Ir1** could be reused 2 times in the same manner without loss of performances (see supporting information).

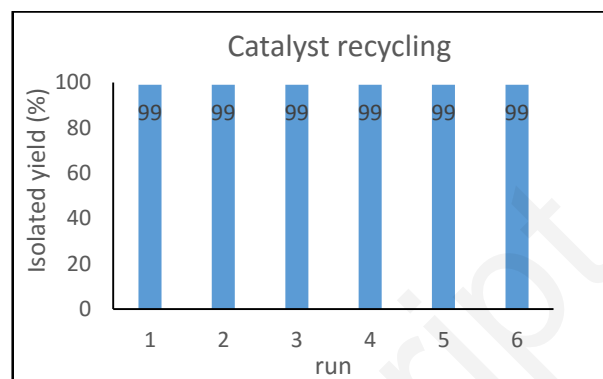
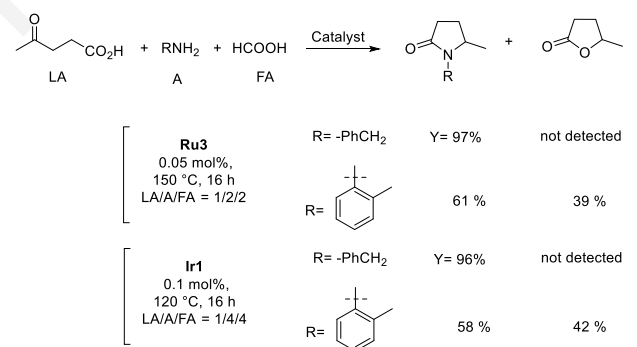


Figure 3 Recycling of **Ru3**

To further extend the scope of these catalysts, they were evaluated in the transfer reductive amination of levulinic acid into 5-methyl-2-pyrrolidinones with benzylamine and the very challenging 2-methylaniline (Scheme 4).²⁰ This reaction was performed with **Ru3** and **Ir1**. In both cases, the benzyl-pyrrolidinone was obtained in high isolated yields, 97% and 96%, respectively. With 2-methylaniline, full conversion of LA was obtained but the reaction mixture consisted in a ~ 60/40 mixture of the desired pyrrolidinone and γ -valerolactone as determined by ¹H NMR. To the best of our knowledge, this is identical to the best result reported so far for this substrate.^{20b}



Scheme 4 Syntheses of pyrrolidinone derivatives

In conclusion we have prepared a series of 4 new cationic ruthenium and iridium complexes bearing dipyriddyamine ligands. These water soluble complexes are highly efficient in the transfer hydrogenation of levulinic acid into γ -valerolactone and for the synthesis of 5-methyl-2-pyrrolidinone derivatives. In both cases (ruthenium and iridium complexes) the catalytic performances were not altered to a large extent or even improved by the introduction of a tertiary amine bridge in the dpa ligand. This feature indicates that an outer sphere mechanism involving the acidic N-H is unlikely although it cannot be totally ruled out for **Ru1** and **Ir1**. The recyclability of a ruthenium complex was demonstrated. Further developments are ongoing to further improve the performances of these dpa-containing catalysts.

SUPPORTING INFORMATION

General Information:

Levulinic acid (98%), formic acid (98%) and 2,2'-dipyridylamine (98%) were purchased from Sigma-Aldrich. Solvents were HPLC grade and used as received. ¹H NMR spectra which were recorded on a Bruker Avance (400 MHz) spectrometer and reported in ppm with reference to CHCl₃ (7.26ppm). Data are reported as follows: s=singlet, d=doublet, t= triplet, q= quartet, m= multiplet. Coupling constants are reported in Hz. ¹³C NMR spectra were recorded at 100 MHz on the same spectrometer and reported in ppm with reference to CDCl₃ (77.16 ppm).

Synthesis of **Ru2**: [(bdpa)(*p*-cymene)RuCl]Cl

2 (0.104 g, 0.4 mmol) was added to a suspension of [RuCl₂(*p*-cymene)]₂ (0.034 g, 0.2 mmol) in methanol (5 mL). The mixture was stirred for 12 h at 50 °C. After evaporation to dryness, the residue was washed with diethylether (3 × 2 mL) to give the expected product obtained as a yellow powder (0.081 g, 85%).

¹H NMR (400 MHz, CDCl₃) δ 8.67 (m, 2H, pyr NCH), 7.76 - 7.71 (m, 2H, CH), 7.38-7.32 (m, 7H, CH), 7.16-7.13 (m, 2H, CH), 5.93 (s, 2H, benzyl CH₂), 5.89 (d, ³J_{H-H} = 6.0 Hz, 2H, *p*-cymene CH), 5.80 (d, ³J_{H-H} = 6.0 Hz, 2H, *p*-cymene CH), 2.78-2.75 (hept, 1H, ³J_{H-H} = 7.6 Hz, *i*Pr CH), 1.81 (s, 3H, CH₃), 1.23 (d, ³J_{H-H} = 7.6 Hz, 6H, *i*Pr CH₃).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ 156.4, 153.5, 140.3, 134.8, 129.2, 127.9, 126.8, 120.4, 116.2, 105.8, 100.8, 86.4, 84.2, 57.4, 30.7, 22.6, 18.0.

Elemental Analysis: Calculated for C₂₇H₂₉N₃Cl₂Ru·H₂O (%): C, 55.38, H, 5.34, N, 7.18. Found: C, 55.45, H, 5.14, N, 7.14.

HRMS (ESI): m/z Calculated for C₂₇H₂₉N₃ClRu: 532.1088; m/z measured: 532.1087

Synthesis of **Ru3**: [(mbdpa)(*p*-cymene)RuCl]Cl

3 (0.11 g, 0.4 mmol) was added to a suspension of [RuCl₂(*p*-cymene)]₂ (0.034 g, 0.2 mmol) in methanol (5 mL). The mixture was stirred for 12 h at 50 °C. After evaporation to dryness, the residue was washed with diethylether (3 × 2 mL) to give the expected product obtained as a yellow powder (0.076 g, Yield: 82%).

¹H NMR (400 MHz, CDCl₃) δ 8.78 (d, ³J_{H-H} = 5.2 Hz, 1H, pyr NCH), 8.64 (d, ³J_{H-H} = 5.6 Hz, 1H, pyr CH), 7.75 (m 1H, CH), 7.63 (m, 1H, pyr CH), 7.37-7.16 (m, 9H, CH), 6.63 (m 1H, CH), 6.12 (d, ³J_{H-H} = 6.0 Hz, 1H, *p*-cymene CH), 5.95 (d, ³J_{H-H} = 6.0 Hz, 1H, *p*-cymene CH), 5.86 (d, ³J_{H-H} = 5.6 Hz, 1H, *p*-cymene CH), 5.82 (d, ³J_{H-H} = 5.6 Hz, 1H, *p*-cymene CH), 2.73-2.67 (hept, ³J_{H-H} = 6.8 Hz, 1H, *i*Pr CH), 2.09 (s, 1.5H, CH₃), 2.11 (s, 1.5H, CH₃), 1.82 (s, 3H, CH₃), 1.29 (d, ³J_{H-H} = 6.8 Hz, 3H, CH₃), 1.27 (d, ³J_{H-H} = 6.8 Hz, 3H, CH₃).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ 158.0, 154.2, 154.1, 152.9, 140.5, 139.7, 138.8, 129.1, 127.7, 126.9, 120.8, 120.7, 118.9, 117.3, 103.9, 103.0, 88.6, 87.4, 83.1, 82.3, 61.9, 30.5, 23.2, 22.1, 21.8, 18.2.

Elemental Analysis: C₂₈H₃₁N₃Cl₂Ru (%): C, 57.83, H, 5.37, N, 7.23. Found: C, 57.68, H, 5.28, N, 7.05.

HRMS (ESI): m/z Calculated for C₂₈H₃₁N₃ClRu: 546.1250; m/z measured: 546.1251

Synthesis of **Ir2**: [(bdpa)Cp*IrCl]Cl

2 (0.031 g, 0.12 mmol) was added to a suspension of [Cp*IrCl₂]₂ (0.045 g, 0.056 mmol) in methanol (5 mL). The mixture was stirred for 12 h at 50 °C. After evaporation to dryness, the residue was washed with diethyl ether (3 × 2 mL) to give the expected product as a yellow powder (0.056 g, yield: 89%).

¹H NMR (400 MHz, CDCl₃) δ 8.54 (d, ³J_{H-H} = 7.2 Hz, 1H, pyr CH), 7.82-7.77 (m, 2H, CH), 7.38-7.35 (m, 5H, CH), 7.28-7.27 (m, 2H, CH), 7.22-7.18 (m, 2H, CH), 5.88 (s, 2H, NCH₂), 1.50 (s, 15H, Cp* CH₃).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ 154.7, 152.3, 141.4, 133.9, 129.3, 128.1, 126.4, 121.8, 116.2, 88.7, 57.4, 8.9.

HRMS (ESI): m/z Calculated for C₂₇H₃₀N₃ClIr: 624.1752; m/z measured: 624.1760

Synthesis of **Ir3**: [(bmdpa)Cp*IrCl]Cl

3 (0.033 g, 0.12 mmol) was added to a suspension of [Cp*IrCl₂]₂ (0.045 g, 0.056 mmol) in methanol (5 mL). The mixture was stirred for 12 h at 50 °C. After evaporation to dryness, the residue was washed with diethyl ether (3 × 2 mL) to give the expected product as a yellow powder (0.092 g, Yield: 86 %).

¹H NMR (400 MHz, CDCl₃) δ 8.61 (dd, ³J_{H-H} = 6.0 Hz, ⁴J_{H-H} = 1.6 Hz, 1H, pyr CH), 8.50 (dd, ³J_{H-H} = 6.0 Hz, ³J_{H-H} = 1.6 Hz, 1H, pyr CH), 7.88-7.84 (m, 1H, CH), 7.71-7.67 (m, 1H, CH), 7.48 (d, ³J_{H-H} = 8.4 Hz, 1H, pyr CH), 7.49-7.30 (m, 6H, CH), 7.21-7.17 (m, 2H, CH), 6.37 (q, ³J_{H-H} = 6.8 Hz, 1H, CH), 1.96 (d, ³J_{H-H} = 6.8 Hz, 3H, CH₃), 1.60 (s, 15H, Cp* CH₃).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ 156.4, 153.6, 152.8, 152.1, 141.8, 139.9, 139.0, 129.2, 128.0, 126.7, 122.4, 121.9, 119.5, 117.2, 88.7, 61.6, 22.1, 9.2.

HRMS (ESI): m/z Calculated for C₂₈H₃₂N₃ClIr: 638.1914; m/z measured: 638.1907

General Experimental Procedure for transfer hydrogenation of Levulinic acid

Levulinic acid (2 mmol), formic acid (2-8 mmol), Et₃N (0-4 mmol), catalyst (0.05-0.1 mol%) were added to a Schlenk tube equipped with a Teflon screw cap. The mixture of substrates and catalyst was heated to the desired temperature in less than 15 min. The crude mixtures were analyzed by ¹H NMR using anisole as internal standard. Volatile compounds were removed under vacuum and the crude product was purified by column chromatography using petroleum ether / ethyl acetate (3/1; v/v) as eluent.

General procedure for the reductive amination of Levulinic acid

Benzylamine (4-8 mmol), catalyst (0.05-0.1 mol%), levulinic acid (2-4 mmol), formic acid (4-8 mmol) and a magnetic stirring bar were placed in a Schlenk tube. The mixture was stirred at 120-150 °C for 16 h. After cooling to room temperature, the reaction was basified with saturated NaOH solution, and extracted with DCM (10 × 3 mL). The organic layers were washed with brine and dried over Na₂SO₄. After removing DCM in vacuo, the product was purified by flash column chromatography using petroleum ether and ethyl acetate (3/1; v/v) with 1% triethylamine as eluent.

The Supporting Information (experimental details, .cif files) is available free of charge on the ACS Publications website.

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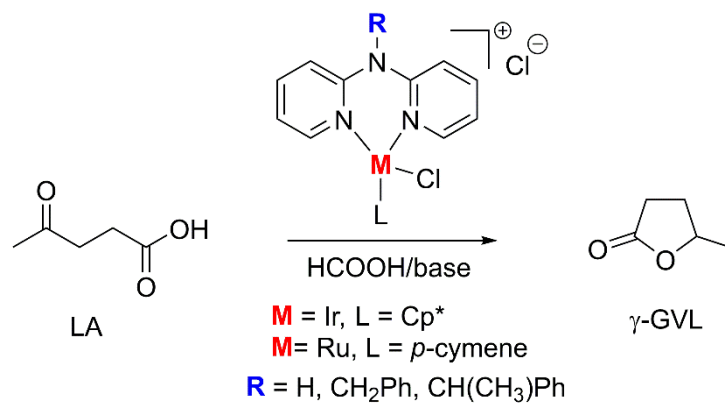
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