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Iridium-Catalyzed Reductive Amination of Levulinic Acid to Pyrrolidinones under H_2 in Water

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The synthesis of pyrrolidinones from reductive amination of levulinic acid (LA) with primary amines is reported. Pyrrolidinones have various applications such as surfactants, pharmaceutical intermediates, dispersants, and solvents. The half-sandwich Cp*Ir complex (Cp* is 1,2,3,4,5-pentamethylcyclopenta-1,3-diene) coordinated by bipyridine ligand bearing both dimethylamino and *ortho*-hydroxyl groups showed high catalytic activity for the reductive amination of LA. A range of primary amines, such as aromatic and benzyl amines, were readily converted to corresponding pyrrolidinones in good yields.

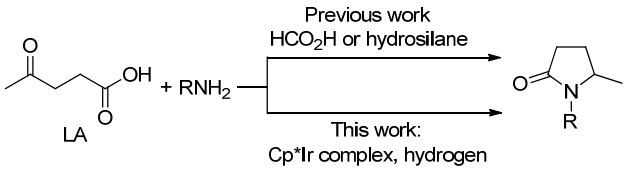
Keywords iridium, reductive amination, hydrogenation, levulinic acid, biomass

Introduction

The abundant and renewable lignocellulosic biomass is an alternative feedstock to fossil resources for the production of specialty fine chemicals. However, the selective transformation of bio-based chemicals to fuels and fine chemicals still faces big challenges. Levulinic acid (LA), a versatile platform chemical from selective hydrolysis of cellulose,[1-5] is regarded as one of the most promising building blocks to produce value-added products.[6-16] For example, γ-valerolactone, a hydrogenation product of LA, can serve as a solvent and precursor to 1,4-pentanediol. Selective hydrogenation of LA can also produce 2-methyltetrahydrofuran, a fuel additive or solvent. The reductive amination of LA can produce pyrrolidinones, which can be applied as surfactants, pharmaceutical intermediates, dispersants, and solvents.

Recently, heterogeneous catalyst,[17-22] including Pd, Rh, Pt, and Au, showed high activity for the reductive amination of LA with various kinds of amines. However, high reaction temperature (>120 ℃) and H_2 pressure are required for the heterogeneous catalysis. In general, pyrrolidinones may be produced through homogeneous catalysis in high selectivity under mild conditions.[23-27] Formic acid, a byproduct generated from the LA production process, is a promising hydrogen source. Fu and coworkers[23] reported the first example of homogeneous Ru-catalyzed reductive amination of LA with aromatic or aliphatic amines by using formic acid. Xiao and coworkers[24] prepared the imine ligand coordinated Cp*Ir complex, and studied the reaction as shown in Scheme 1 using formic acid. They further developed the formic acid assisted reductive amination without catalyst in dimethyl sulfoxide (DMSO).[25] As the silica gel column was used to separate the product from DMSO, separation could be an issue in a large scale synthesis. Hydrosilane was also successfully applied as a hydrogen source for the synthesis of pyrrolidinones from LA. Both boric compound[26] and In complex[27] could efficiently catalyze the reductive amination by using hydrosilane. However, hydrosilane is not an ideal reducing reagent owing to its high price and low atom-economy. Compared with both formic acid and hydrosilane, H_2 is the most atom-economic hydrogen source (Scheme 1). However, homogeneous catalysis for pyrrolidinones synthesis from LA and amines by using H_2 was rarely studied so far.

Scheme 1 Previous work and this work



We previously reported the Cp*Ir complex catalyzed hydrogenation/hydrolysis of bio-based 5-hydroxymethylfurfural by using H_2 as a hydrogen source.[28-30] In that work, the product 1-hydroxyhexane-2,5-dione was con-

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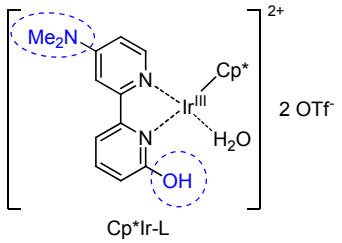
In Memory of Professor Enze Min.

sidered as a potential platform to produce value-added chemicals. The impact of bipyridine ligand's structure on the activity of Cp*Ir complex was systematically researched. The hydrogenation rate extremely increased when the bipyridine ligand was modified by both dimethylamino (NMe_2) and *ortho*-hydroxyl groups (*o*-OH) (Scheme 2). The *o*-OH group assisted the H_2 heterolytic dissociation,[31-43] and the electron-donating ability of both NMe_2 and *o*-OH increased the hydrogenation activity of the Cp*Ir-L complex. In this work, we investigated the reductive amination of LA by Cp*Ir-L complex under H_2 atmosphere.

Scheme 2 Structure of Cp*Ir-L complex of this work. OTf is trifluoromethanesulfonate



Cp*Ir-L

Experimental

General methods

NMR spectra were run in $CDCl_3$ on a 400 MHz instrument and recorded at the following frequencies: proton (^{1}H, 400 MHz), carbon (^{13}C, 100 MHz). ^{1}H NMR chemical shifts were reported using tetramethylsilane (TMS) as the internal standard. ^{13}C NMR spectra were reported using $CDCl_3$ as the internal standard.

Preparation of Cp*Ir-L

The Cp*Ir-L was prepared according to the literature.[30] ^{1}H NMR (400 MHz, CD_3OD) δ: 1.65 (s, 15H), 3.29 (s, 6H), 7.02—7.05 (m, 1H), 7.21—7.23 (m, 1H), 7.58 (d, J=2.88 Hz, 1H), 8.09—8.13 (m, 2H), 8.53 (d, J=6.96 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ: 8.1, 38.6, 88.8, 105.8, 109.9, 113.3, 114.8, 120.4 (q, J=317 Hz), 143.6, 149.6, 154.5, 155.9, 156.1, 163.9.

Synthesis of pyrrolidinone 2

To a solution of LA (162.4 mg, 1.4 mmol) in water (2.0 mL) at room temperature was added Cp*Ir catalyst (0.43 mg, 0.0005 mmol) and aniline (1.0 mmol). The high pressure reactor (20 mL) was purged with H_2 (20 bar) four times, and was heated to 80 ℃ for 10 h. The aqueous solution was extracted by CH_2Cl_2 (5.0 mL) three times. After removing the combined CH_2Cl_2, the crude residue was purified on a silica gel column to afford the product **2**.

5-Methyl-1-phenylpyrrolidin-2-one (**2a**, 166.3 mg, 95%).[25] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 7.41—7.36 (m, 4H), 7.22—7.18 (m, 1H), 4.33—4.27 (m, 1H), 2.68—2.49 (m, 1H), 2.41—2.32 (m, 1H), 1.79—1.70 (m, 1H), 1.21—1.19 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.2, 137.6, 129.0, 125.7, 124.0, 55.6, 31.4, 26.8, 20.2.

5-Methyl-1-(*p*-tolyl)pyrrolidin-2-one (**2b**, 179.8 mg, 95%):[25] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 7.24—7.17 (m, 4H), 4.28—4.19 (m, 1H), 2.66—2.47 (m, 2H), 2.40—2.30 (m, 4H), 1.78—1.68 (m, 1H), 1.19—1.17 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.2, 135.6, 135.0, 129.6, 124.2, 55.8, 31.3, 26.8, 21.0, 20.2.

1-(4-Methoxyphenyl)-5-methylpyrrolidin-2-one (**2c**, 191.0 mg, 93%):[25] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 7.25—7.21 (m, 2H), 6.93—6.89 (m, 2H), 4.21—4.13 (m, 1H), 3.78 (s, 1H), 2.63—2.46 (m, 2H), 2.38—2.28 (m, 1H), 1.76—1.67 (m, 1H), 1.15 (d, J=6.24 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.1, 157.5, 130.3, 125.9, 114.2, 55.9, 55.3, 31.0, 26.7, 20.1.

1-(4-Fluorophenyl)-5-methylpyrrolidin-2-one (**2d**, 173.5 mg, 90%):[25] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 7.35—7.29 (m, 2H), 7.10—7.04 (m, 2H), 4.27—4.19 (m, 1H), 2.66—2.48 (m, 2H), 2.40—2.32 (m, 1H), 1.79—1.70 (m, 1H), 1.18 (d, J=6.24 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.3, 160.4 (d, J=244 Hz), 133.5 (d, J=3 Hz), 126.0 (d, J=8 Hz), 115.8 (d, J=22 Hz), 55.9, 31.2, 26.7, 20.1.

1-(4-Chlorophenyl)-5-methylpyrrolidin-2-one (**2e**, 187.0 mg, 89%):[25] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 7.36—7.31 (m, 4H), 4.30—4.22 (m, 1H), 2.66—2.46 (m, 2H), 2.39—2.30 (m, 1H), 1.78—1.69 (m, 1H), 1.19 (d, J=6.24 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.1, 136.2, 130.6, 128.9, 124.8, 55.3, 31.2, 26.5, 19.9.

1-(4-Bromophenyl)-5-methylpyrrolidin-2-one (**2f**, 223.6 mg, 88%):[25] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 7.51—7.47 (m, 2H), 7.31—7.28 (m, 2H), 4.32—4.24 (m, 1H), 2.67—2.48 (m, 2H), 2.41—2.32 (m, 1H), 1.79—1.71 (m, 1H), 1.20 (d, J=6.24 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.2, 136.8, 132.1, 125.2, 118.7, 55.4, 31.3, 26.6, 20.0.

Ethyl 4-(2-methyl-5-oxopyrrolidin-1-yl)benzoate (**2g**, 160.7 mg, 65%):[25] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 8.08—8.04 (m, 2H), 7.57—7.54 (m, 2H), 4.45—4.34 (m, 3H), 2.73—2.51 (m, 2H), 2.43—2.35 (m, 1H), 1.88—1.74 (m, 1H), 1.39 (t, J=7.12 Hz, 3H), 1.26 (d, J=6.24 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4, 166.2, 141.9, 130.5, 126.8, 122.0, 61.0, 55.1, 31.5, 26.5, 19.9, 14.4.

1-(4-Benzylphenyl)-5-methylpyrrolidin-2-one (**2i**, 217.5 mg, 82%):[25] ^{1}H NMR (400 MHz, D_2O) δ: 7.50—7.45 (m, 5H), 4.26—4.16 (m, 2H), 3.36—3.28 (m, 1H), 2.40—2.21 (m, 2H), 2.07—1.98 (m, 1H), 1.84—1.75 (m, 1H), 1.36 (t, J=6.64 Hz, 3H); ^{13}C NMR (100 MHz, D_2O) δ: 181.4, 131.2, 129.6, 129.5, 129.3, 54.4, 48.4, 33.6, 29.0, 15.5.

1-Butyl-5-methylpyrrolidin-2-one (**2j**, 97.8 mg, 63%):[27] ^{1}H NMR (400 MHz, D_2O) δ: 3.10—2.97 (m, 2H), 2.75—2.36 (m, 3H), 2.02—1.66 (m, 4H), 1.42—1.34 (m, 5H), 0.96 (t, J=6.64 Hz, 3H); ^{13}C NMR (100 MHz, D_2O) δ: 179.4, 55.1, 44.5, 35.7, 29.4, 28.4, 20.2, 17.3, 13.7.

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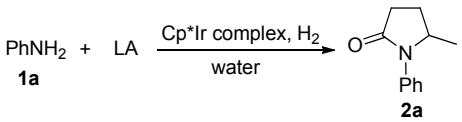
Results and Discussion

Because water was environmentally friendly and the desired product **2a** could easily be separated from water through extraction, the optimization of LA with aniline was carried out in aqueous solution (Table 1). The reductive amination of aniline with LA was firstly optimized under 20 bar of H_2 at 80 ℃, and 75% of **2a** was isolated (Entry 1). Compared to the result of Entry 1, the yield of **2a** decreased at lower H_2 pressure (60%, Entry 2), while the yield of **2a** was slightly increased with increasing H_2 pressure from 20 bar (75%, Entry 1) to 25 bar (77%, Entry 3). Thus, the subsequent optimizations were carried out under 20 bar of H_2. As the byproduct γ-valerolactone can consume a small amount of LA, the excess amount of LA was optimized. The yield of **2a** reached 95% when 1.4 equiv. of LA was used (Entry 5). The yield of **2a** decreased to 85% when the temperature was increased to 100 ℃ (Entry 6), because the γ-valerolactone formation rate probably increased faster than the reductive amination rate with increasing the temperature. The yield of **2a** decreased to 43% when the temperature was decreased to 60 ℃ (Entry 7). In the presence of 1.4 equiv. of LA, the yield of **2a** decreased to 83% with lower pressure of H_2 (15 bar, Entry 8), while the yield of **2a** did not significantly increased with higher pressure of H_2 (20 bar, Entry 9). Finally, the reductive amination of LA was studied in the presence of a small amount of Cp*Ir-L, and the turnover number (TON) of catalyst reached 8800 (Entry 7). The subsequent synthesis of pyrrolidinones from LA and various amines was performed with Cp*Ir-L as the catalyst in water at 80 ℃ under a H_2 atmosphere (Entry 5).

Table 1 Optimization of reaction conditions[a]



Entry	Temperature/℃	LA (equiv.)	Pressure/bar	Yield[b]/%
1	80	1.0	20	75
2	80	1.0	15	60
3	80	1.0	25	77
4	80	1.2	20	89
5	80	1.4	20	95
6	100	1.4	20	89
7	60	1.4	20	43
8	80	1.4	15	83
9	80	1.4	25	96
10[c]	80	1.4	20	88

[a] Reaction conditions: LA, aniline (1.0 mmol), water (2.0 mL), and Cp*Ir-L (0.05 mol%), under H_2, for 10 h. [b] Isolated yields were given. [c] Cp*Ir-L (0.01 mol%), and for 24 h.

The direct reductive amination of LA with various amines was performed under optimized conditions. The results are shown in Table 2. The aromatic amines with electron-donating methyl or methoxyl groups smoothly proceeded to generate the corresponding products **2b** and **2c** in high yields (95% and 93%). Good yields of **2d**, **2e**, and **2f** (90%, 89%, and 88%, respectively) were also obtained when the amines bore with electron-withdrawing groups. Compared to the amines with electron-donating groups (Me and OMe), the amines with electron-withdrawing groups (F, Cl, and Br) required longer reaction time to achieve high yields. The electron-withdrawing groups probably slowed down the imination of amines with LA, resulting in a longer time for electron-deficient amines to convert. The low yields of **2g** (65%) and **2h** (0%) were owing to the strong electron-withdrawing effects of CO_2Et and CN, respectively. We also tried the reductive amination of LA with benzyl amine, and the product **2i** was obtained with an 82% isolated yield. The product **2j** was obtained with a 63% isolated yield, while none of product **2k** was obtained probably because of the steric hindrance effect. The product **2l** was also not obtained.

Based on the literatures [30,37] and experiments, the proposed mechanism of Cp*Ir-L catalyzed reductive amination is shown in Scheme 4. The Cp*Ir-L first releases a proton to form intermediate **A**, followed by H_2 heterolytic dissociation on **A** to form intermediate **B**. The imination of LA with amine generates imine product **C**. **C** reacts with **B** through an 8-membered ring transition state[30,44,45] **D** to form **E** and **A'**. The intramolecular amidation of **E** produces the product. **A'** resonates to form **B** to undergo the next catalytic cycle. The amine with electron-withdrawing groups might slow down the formation rate of **C**, resulting in a low reactive-

Scheme 4 Proposed reductive amination mechanism

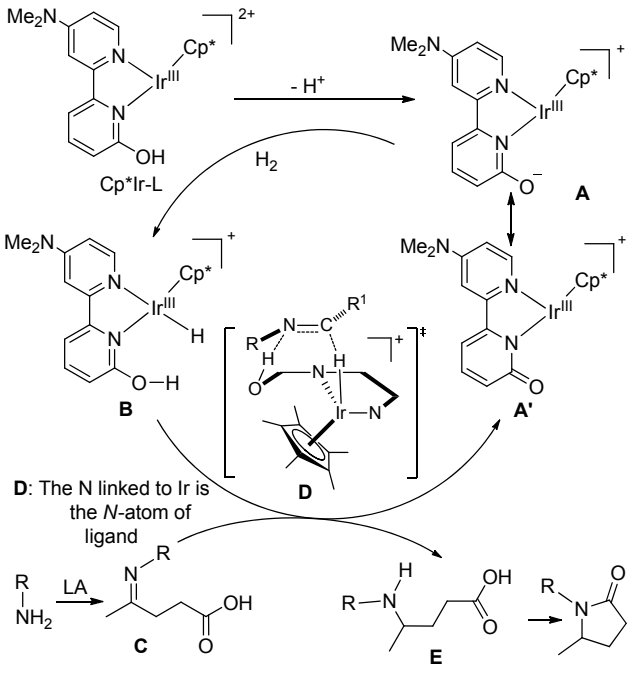
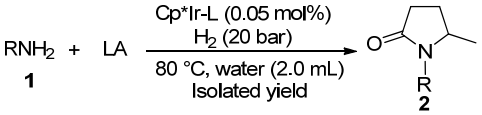
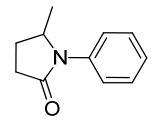
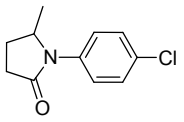
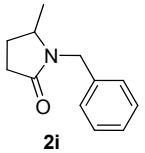
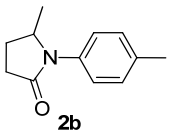
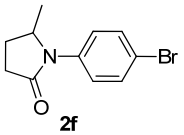
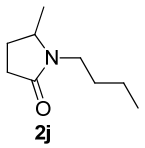
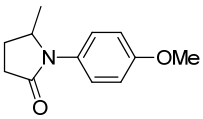
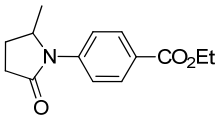
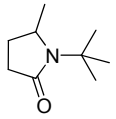
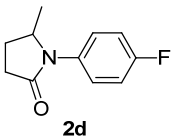
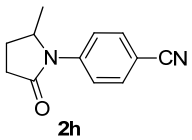
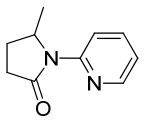


Table 1 Reaction of LA with different amines[a]



Compd.	Time/h	Yield/%	Compd.	Time/h	Yield/%	Compd.	Time/h	Yield/%
 **2a**	10	95	 **2e**	16	89	 **2i**	10	82
 **2b**	7	95	 **2f**	14	88	 **2j**	24	63
 **2c**	9	93	 **2g**	12	65	 **2k**	24	0
 **2d**	16	90	 **2h**	16	0	 **2l**	24	0

[a] Isolated yields were given for all products.

ity of the relative amines.

Conclusions

In summary, we developed a simple and efficient procedure to synthesize pyrrolidinones by Cp*Ir complex catalyzed reductive amination of LA with amines under H_2 in water. Aromatic amines bearing electron-donating groups show good reactivity and yield to form the corresponding pyrrolidinones, while the aromatic amines bearing electron-withdrawing groups require longer time to reach good yields. Further extension of substrate scope and the research on the catalyst recycle, as well as the large scale synthesis, are underway.

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