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Synthesis, structure, characterization and one pot catalytic activity of half-sandwich iridium(III) complexes

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ABSTRACT

A series of stable mononuclear half-sandwich iridium(III) complexes of the general formula $[(\eta^5\text{-}C_5Me_5)Ir(L)Cl](BPh_4)$ has been synthesized in dry methanol using different imino pyridine ligands (L_1–L_6) and $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu\text{-}Cl)_2Cl_2]$ in a 2:1 molar ratio. All complexes were fully characterized by melting point, CHN analysis, FT-IR, UV–visible, ^1H NMR, ^{13}C NMR spectroscopy and mass spectrometry. The structure of complex **3** $[(\eta^5\text{-}C_5Me_5)Ir(L_3)Cl](BPh_4)$ was determined by single crystal X-ray structure analysis, showing a chelating coordination mode of the imino pyridine L_3. One pot organic transformations of aldehyde to amide were carried out by complexes **1–6** in toluene at 110 °C in the presence of hydroxyl amine hydrochloride and sodium bicarbonate. The catalytic activity of complex **3** was found to be excellent, showing high conversion with catalytic turnover frequency up to 500.

1. Introduction

Amide functional group is one of the most important organic functions, which is widely used in synthetic organic chemistry, biochemistry, medicine and materials science. Amides and their derivatives are valuable starting materials for the synthesis of proteins, polymers, detergents, lubricants, as well as agrochemical and pharmaceutical compounds [1,2]. Furthermore, physical and chemical properties of amides, such as high polarity, chemical stability and conformational diversity, make it one of the most popular and reliable functional groups in organic chemistry [3,4]. Amides can be synthesized from various starting materials like acids [5–7], acid chlorides [8], alcohols [9–11], aldehydes [12,13], azides [14], esters [15], isocyanates [16], nitriles [17–19], nitrobenzenes [20] and oximes [21,22]. These transformations are stoichiometric reactions, requiring an activating or coupling reagent under relatively harsh reaction conditions, and often result in the production of huge amounts of by-products [23].

Transition metal catalysts built from scandium [24], titanium [25], zirconium [26], vanadium [27], chromium [28], manganese [29], iron [30], cobalt [31], nickel [32], copper [33,34], ruthenium [35–38], rhodium [39], palladium [40], iridium [41], platinum [42] and silver [43] have been reported for the Beckmann rearrangement (Scheme 1): A traditional method for the synthesis of amide from various ketones or ketoximes in the presence of a Lewis acid catalyst. However, this catalytic reaction often requires large amount of the catalyst and high temperature, thus limiting their applications [44,45].

As previously mentioned, traditional routes to amides often use hazardous, toxic coupling reagents, and they are associated with the production of stoichiometric amount of waste products, which makes it difficult to synthesize primary amides from aldoximes or aldehydes [46]. To circumvent these limitations, alternative methods for amide synthesis with high efficiency, broad substrate scope and mild conditions are in great demand. The direct oxidative amidation of aldehydes into amides by means of one-pot processes has been identified as a powerful alternative (Scheme 2). The method is of synthetic interest because of the following reasons: (i) Starting materials are commercially available; (ii) The process involves simple chemicals; (iii) The reaction is carried out under mild conditions and environmentally friendly; (iv)

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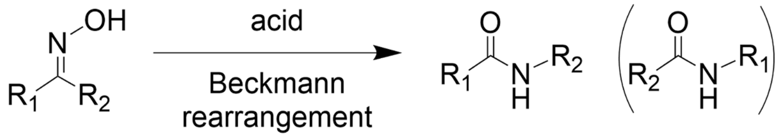
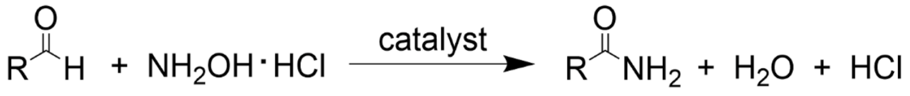
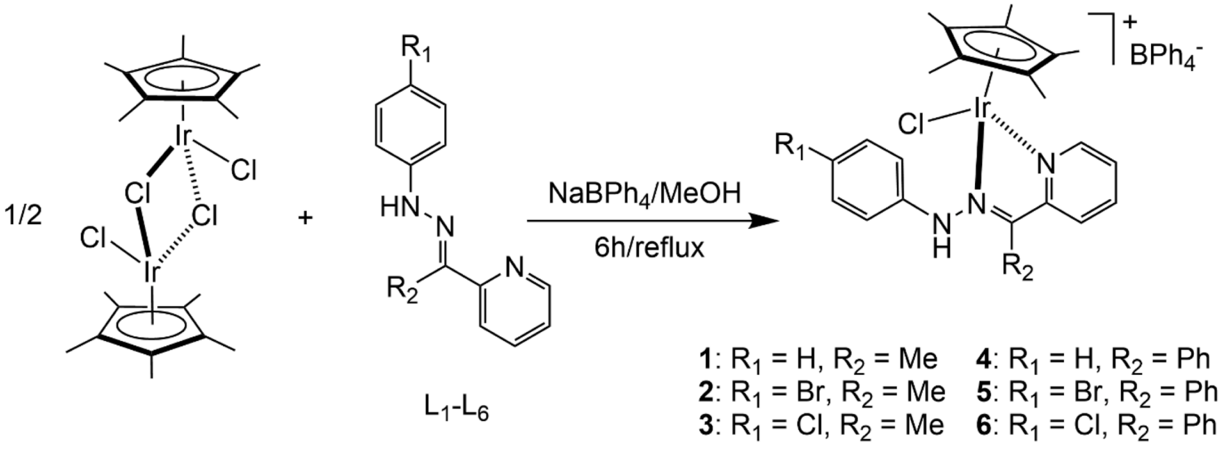


Scheme 1. Beckmann rearrangement of oximes to amides (second isomer in brackets).



Scheme 2. Metal catalyzed reactions of aldehydes to amides.



Scheme 3. Synthesis of half-sandwich iridium(III) complexes **1**–**6**.

Limited by-products production.

Recently, more effort has been devoted to the investigation of half-sandwich complexes as catalysts for the one-pot synthesis of primary amides from hydroxylamine hydrochloride and aldehydes through the in situ rearrangement of aldoximes [47,48]. Among them, the iridium catalysts are having less reports and remain rare [49]. Therefore, we have synthesized iridium complexes with imino pyridine ligands. The complexes have been characterized by spectral and analytical methods, and for complex **3** by single crystal X-ray structure analysis. All complexes were tested for their catalytic activity on amide formation

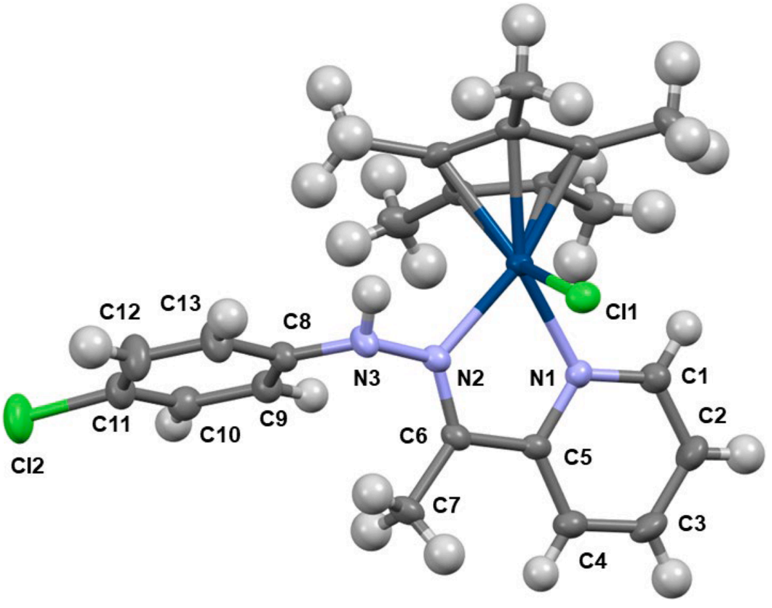
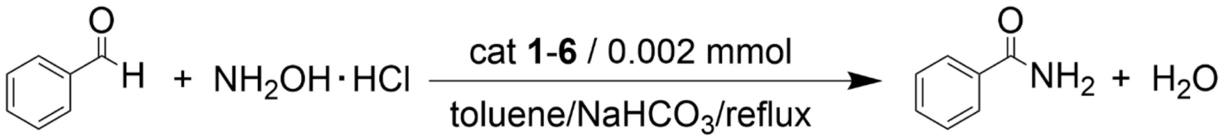


Fig. 1. Molecular structure of $[(\eta^5\text{-}C_5Me_5)Ir(L_3)Cl]^+$ showing the labeling scheme, and with BPh_4^- being omitted for clarity. Selected bond lengths (Å) and angles (°): Ir-Cl1 2.4138(6), Ir-N1 2.0904(18), Ir-N2 2.0772(19), N2-N3 1.395(3), N3-C8 1.409(3), N1-C5 1.366(3), C5-C6 1.462(4), N2-C6 1.299(3); N1-Ir-N2 75.89(8), N1-Ir-Cl1 75.89(8), N2-Ir-Cl1 75.89(8), C6-N2-N3 118.7(2), N2-N3-C8 121.9(2), C5-C6-N2 113.6(2).



Scheme 4. Organic transformation of benzaldehyde to benzamide.

reactions.

2. Results and discussion

A series of half-sandwich iridium(III) complexes has been synthesized in dry methanol from the starting precursor $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu\text{-}Cl)_2Cl_2]$ and imino pyridine ligands (L_1–L_6), in the presence of tetraphenylborate in a 1:2:2 molar ratio (Scheme 3). All complexes are air-stable, non-hygroscopic in nature, partially soluble in water and highly soluble in polar solvents such as chloroform, dichloromethane, acetonitrile and dimethyl sulfoxide, producing intense green solutions. All complexes are found to be diamagnetic, low spin complexes, and have been characterized by CHN analysis, FT-IR, UV-visible, ^{1}H NMR, ^{13}C NMR spectroscopy and mass spectrometry (See experimental part).

The IR spectra of the imino pyridinyl iridium(III) complexes were compared to the imino pyridine ligands, in order to determine the probable mode of coordination to the metal center. The free hydrazone ligand showed a strong band at around 1600–1617 cm^{-1} assigned to the azomethine nitrogen vibration $\nu_{(C\,=\,N)}$. After coordination to iridium, this band is shifted to lower wavenumber (1579–1597 cm^{-1}), indicating that the azomethine nitrogen atom is coordinated to the metal [48,50]. Additionally, all complexes show a medium intensity band in the region 1020–1030 cm^{-1}, corresponding to the coordination of a pyridyl nitrogen atom [51], thus suggesting a *N,N'*-chelating coordination mode.

The electronic spectra of the iridium complexes **1**–**6** were recorded in dichloromethane (10^{-4} M concentration) at room temperature, showing two to three bands in the 800–200 nm range. The low energy absorption band observed in the range of 333 to 373 nm is assigned to MLCT transitions, while the high energy absorption band observed between 206 and 290 nm is assigned to ligand-centered $n\rightarrow\pi^*/\pi\rightarrow\pi^*$ transitions, which is consistent with analogous complexes [52].

The ^{1}H NMR spectra of the complexes have been recorded in CD_3CN solutions. Each complex shows multiplet at 6.85–8.85 ppm due to the presence of the aromatic protons of the ligands. Most of the signals associated to the coordinated phenyl hydrazone ligand were clearly observed, however a few could not be isolated due to overlap with the BPh_4 anion. In addition, the methyl proton appeared as a sharp singlet around 2.02–2.70 ppm for complexes **1**–**3**, while the NH protons appeared as a broad singlet in the region 7.80–10.44 ppm. The cyclopentadienyl (cp*) protons appeared as a sharp singlet around 1.5 ppm, denoting that the five methyl groups are poorly affected by ligand complexation. The NMR reveals that all complexes are having a cp* group, aromatic ligand containing uncoordinated NH group and a methyl group for complexes **1, 2** and **3**, which confirms the expected structures (Scheme 3). The ESI-MS (positive mode) spectra of all iridium salts (**1–6**) displayed a molecular ion peak, which correspond to the cationic complexes $[(\eta^5\text{-}C_5Me_5)Ir(L_{1-6})Cl]^+$.

The molecular structure of **3** was confirmed by single-crystal X-ray structure analysis. The complex is displayed in Fig. 1. The crystallographic data are summarized in Table S1, while selected bond lengths and angles are provided in the caption of Fig. 1. The salt crystallized in the centro-symmetric space group *P*-1, with two cationic complexes and two tetraphenylborate anions per asymmetric unit, thus confirming the racemic nature of the chiral-at-the-metal complex. The complex shows a typical piano-stool structure, with standard geometric parameters and bond lengths. The bite angle of the chelating N1-Ir1-N2 is 75.89(8)°, while the bond lengths of N1-Ir1 and N2-Ir1 are normal at 2.090(2) and 2.077(2) Å, respectively. The metal to chloride bond length is 2.4138(6) Å. Upon coordination, the angle between the planes of the pyridyl and chloro-phenyl groups is 64.4°. A strong hydrogen bond between the hydrogen atom of the N—H group of one enantiomer and the coordinated chloride atom of the second enantiomer is observed, having a Cl···H distance of 2.56 Å and a N—H···Cl angle of 123.1°. Overall, the complex shows structural characteristics similar to those of previously reported half-sandwich iridium(III) analogues [53].

Table 1
Catalytic activity of complexes **1**–**6** with benzaldehyde.[a]

Complex	1h	2h	4h	6h	8h	10h	12h
1	40	45	50	53	57	61	64
2	62	67	70	72	75	77	79
3	80	92	92	92	93	93	95
4	30	41	45	46	52	56	60
5	59	62	64	67	70	72	75
6	70	76	77	79	83	86	90

[a] Conditions: Mixtures of benzaldehyde (1 mmol), $NH_2OH{\bullet}HCl$ (1 mmol), $NaHCO_3$ (1 mmol), catalyst (0.002 mmol) in toluene (2 ml) at refluxed for 2 h. Conversion of product was determined using ^{1}H NMR (integrations of $H_{aldehyde}$ vs H_{amide}).

Table 2
Effect of catalyst/substrate ratios (C/S).[a]

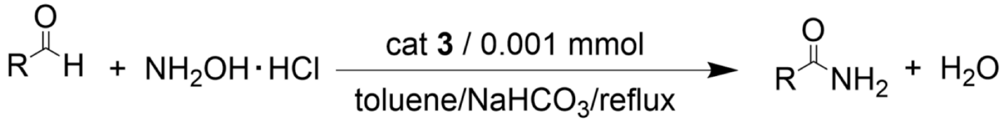
Entry	Catalyst / Substrate	Yield[b](%)
1	1:100	91
2	1:200	90
3	1:300	92
4	1:500	92
5	1:1000	96
6	1:1500	80
7	1:2000	65

[a] Conditions: Reactions were carried out at 110 °C using benzaldehyde (1 mmol), $NH_2OH{\bullet}HCl$ (1 mmol), $NaHCO_3$ (0.4 mmol), catalyst **3** (0.01–0.0005 mmol) in toluene (2 ml) and refluxed for 2 h. [b] Yield was determined using ^{1}H NMR (integrations of $H_{aldehyde}$ vs H_{amide}).

Iridium mediated amidation reactions involve an aldehyde and hydroxylamine hydrochloride (Scheme 4). For optimization of the reaction conditions, the formation of benzamide from benzaldehyde and hydroxylamine hydrochloride in toluene was selected as a control experiment, in agreement with our previous publication [46]. For this initial optimization, the catalytic efficiency of complexes **1**–**6** was investigated from 1 to 12 h (Table 1). Noteworthy, complex **3** attained 95 % yield of benzamide after 12 h, but was already at 92 % yield after 2 h, which is an exception among the complexes. The second-best catalyst was complex **6**, giving a similar yield after 12 h, followed by complexes **2** and **5** with 79 and 75 % yield, respectively. Interestingly, the presence of a chloro (L_3, L_6) or bromo (L_2, L_5) substituent on L appears to play a positive role in the conversion of aldehyde to amide. The catalytic activity of the complexes was in the order **3** > **6** > **2** > **5** > **1** > **4**. Complex **3** (followed by complex **6** has provided a superior yield than the other complexes, which seems to be linked to the presence of the chloro-substituent, and therefore, complex **3** was prioritized in our study.

Control experiments were performed, following the same protocol, using $IrCl_3{\cdot}nH_2O$, the imino pyridine alone, or mixtures of $IrCl_3{\cdot}nH_2O$ and ligands, all showing no catalytic reaction. This confirm the catalytic role of the half-sandwich iridium(III) complexes **1**–**6**. The next

Table 3
One pot conversion of aldehydes to amides using complex **3**.[a]



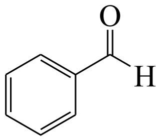
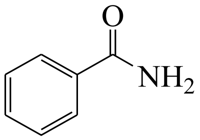
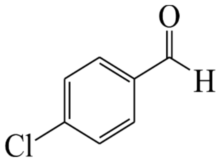
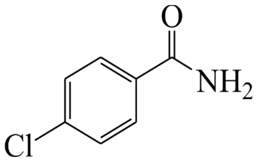
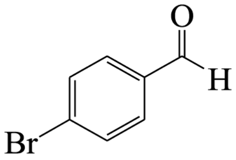
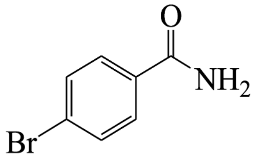
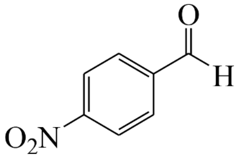
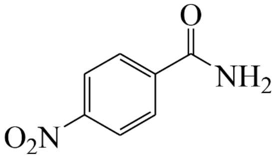
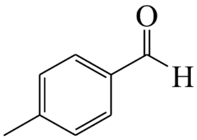
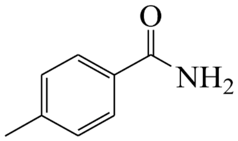
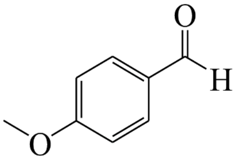
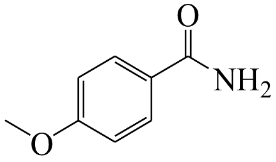
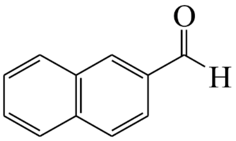
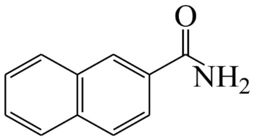
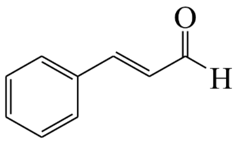
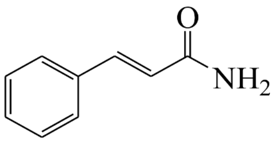
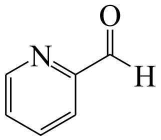
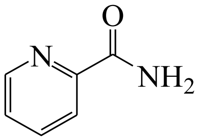
Entry	Aldehyde	Amide	Yield[b]	TON[c]	TOF[d]
1			92	920	460
2			98	980	490
3			99	990	495
4			96	960	480
5			85	850	425
6			87	870	435
7			90	900	450
8			98	980	490
9			97	970	485

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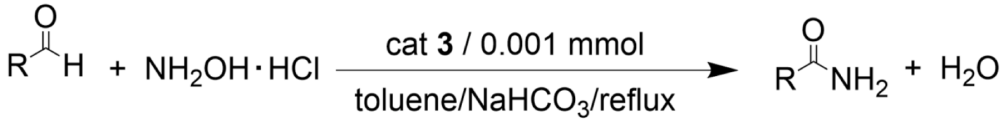
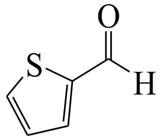
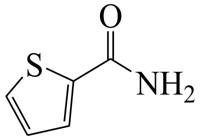
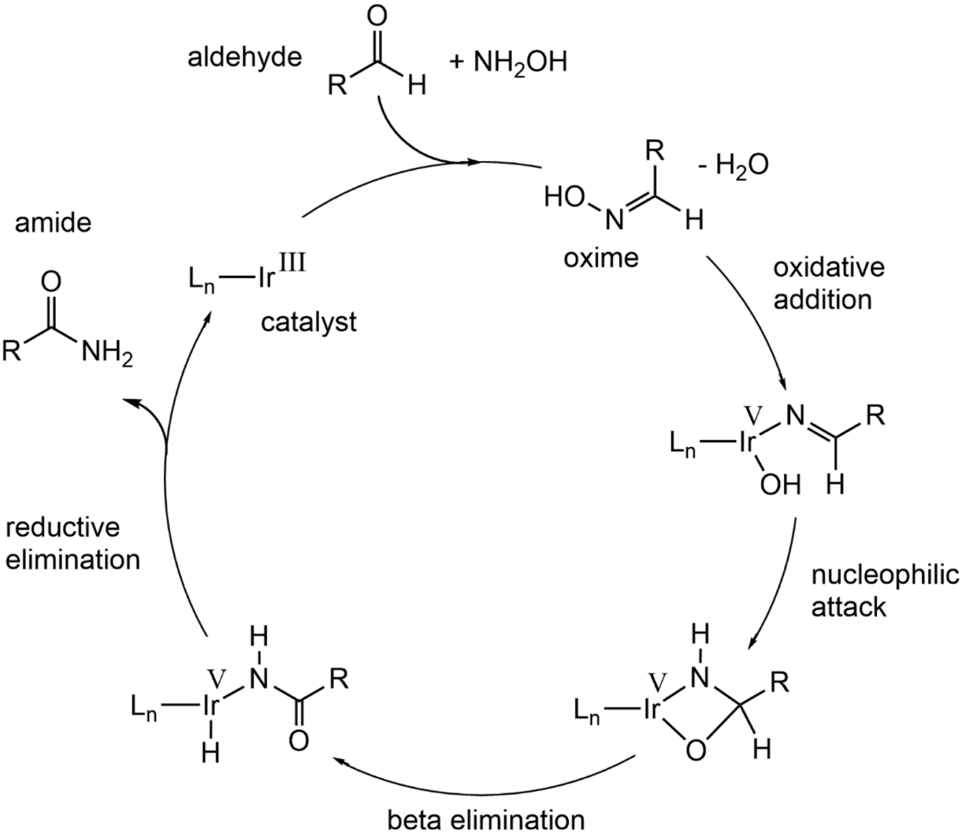
Table 3 (*continued*)



Entry	Aldehyde	Amide	Yield[b]	TON[c]	TOF[d]
10			100	1000	500

[a] Aldehyde (1 mmol), NH_2OH•HCl (1 mmol), $NaHCO_3$ (1 mmol), catalyst (0.001 mmol) and toluene (2 ml) at refluxed for 2 h. [b]Isolated yield after column chromatography and yield determined by ^{1}H NMR (integrations of $H_{aldehyde}$ vs H_{amide}). Catalyst/Substrate/Base ratio 1:1000:2.5. [c]TON = moles of product on moles of catalyst. [d]TOF = TON h^{-1}.



Scheme 5. Proposed mechanism for the transformation of aldehydes to amides from an Ir(III) catalyst.

optimization experiment was carried out with benzaldehyde, varying the catalyst/benzaldehyde ratio (C/*S* = catalyst/substrate). Successive C/S ratios of 1:100, 1:200, 1:500, 1:1000, 1:1500 and 1:2000 were tested, and the yields obtained are presented in Table 2. From the table, it was observed that 1:100, 1:200 and 1:500 ratios showed very good conversion. On increasing the C/S ratio to 1:500 and 1:1000, the reaction proceeded with even better conversions, while it starts to decrease with 1:1500 and 1:2000. Therefore, it appears that the 1:1000 C/S ratio provides the highest yield and accordingly the following conditions were used for the next set of experiments: 1:1000 catalyst/aldehyde ratio, in the presence of NH_2OH•HCl and $NaHCO_3$, in toluene at 110 °C.

Then, we applied these optimized reaction conditions with various aromatic aldehydes, and the corresponding yields are presented in Table 3. Benzaldehyde was converted into benzamide with 92 % conversion (entry 1). Halogen-substituted aromatic shows an enhancing effect on the catalytic activity, which is expressed by the quantitative formation of the corresponding amides. 4-Bromo and 4-chloro benzaldehydes gave 99 and 98 % yield, respectively (entries 2 & 3). This suggests that electron withdrawing groups increase the formation of amides. Similarly, the 4-nitro substituent on benzaldehyde imparts a major role (entry 4), showing an excellent yield. On the other hand, methyl and methoxy substituted benzaldehydes gave 85 and 87 % yield respectively, showing a less efficient process (entries 5 & 6). To summarize, electron-withdrawing groups on benzaldehyde increased the catalytic activity, while electron donating groups decreased the yield. The order of reactivity for 4-substituted benzaldehydes is Br > Cl > NO_2 > H > OCH_3 > CH_3. When conjugation is added to benzaldehyde in 3 & 4 positions, the yield is 90 % due to a resonance effect (entry 7). For 1-cinnamaldehyde the yield is 98% of the corresponding amide (entry 8). The introduction of hetero atom in the ring also increased the yield. The pyridine-2-carboxaldehyde gave 97 % of the corresponding amide (entry 9). And the thiophene-2-carboxaldehyde gave total conversion of thiophene-2-carboxamide (entry 10).

Mechanistically, it is believed that the catalytic transformation proceeds concertedly via classical Beckmann rearrangement, forming initially the corresponding oxime. Then, the Lewis acid catalyst (the Ir (III) complex) attacks this oxime, to generate the amide. Therefore, based on previous reports [37,46], a catalytic cycle can be proposed (Scheme 5). In this cycle, the aldoxime is formed first by the reaction of the aldehyde and hydroxylamine hydrochloride in the presence of sodium bicarbonate. In the second step, the Ir(III) complex undergoes an oxidative addition reaction with the oxime to form Ir(V) species, followed by a nucleophilic attack on the coordinated imine, then beta-elimination of the cyclometallated complex, before the reductive elimination that provides the corresponding amide and regeneration of the Ir(III) catalyst. It can be observed that during the course of the reaction, nitrile is not eliminated.

3. Conclusion

Six half-sandwich iridium complexes were synthesized and characterized by spectral and analytical methods. Among the six complexes, complex **3** was structurally confirmed by single-crystal X-ray structure analysis, and this complex showed the best catalytic activity, reaching quantitative formations of 4-bromobenzamide and thiophene-2-carboxamide in the presence of NH_2OH•HCl and $NaHCO_3$ in toluene at reflux. For all tested aldehydes, the turnover numbers are > 870, thus suggesting that such Ir(III) catalysts are good candidates for the one pot synthesis of amides from aldehydes.

4. Experimental methods

4.1. Materials and methods

The chemicals $IrCl_3{\cdot}nH_2O$, 1,2,3,4,5-pentamethylcyclopentadiene, hydroxylamine hydrochloride, phenyl hydrazine, 1-bromo phenyl hydrazine, 1-chloro phenyl hydrazine, 2-acetyl pyridine, 2-benzoyl pyridine, benzaldehyde, 2-naphthaldehyde, 4-anisaldehyde, trans-cinnamaldehyde, 2-thiophenecarboxaldehyde and sodium bicarbonate were purchased from Sigma Aldrich. 4-Nitrobenzaldehyde and 4-tolylaldehyde were obtained from Fluka and 4-bromobenzaldehyde from Acros. All reagents were of analytical reagent grade and used as received. The starting materials $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu\text{-}Cl)_2Cl_2]$ and the ligand were prepared according to published methods [54,55]. Infrared spectra were recorded in the range of 4000–400 cm^{-1} on a Perkin-Elmer FTIR 1720 X spectrophotometer with the sample prepared as KBr pellets. The ^1H NMR spectra were recorded with a Bruker Avance II 400 MHz spectrometer in CD_3CN for complexes using TMS as an internal standard. Melting points were recorded with a Boetius micro-heating table and were uncorrected. The elemental CHN microanalysis content of samples was determined at STIC, Cochin University of Science and Technology, Cochin, by analytic function on a VarioEL III CHNS elemental analyzer. Electronic spectra of the complexes in dichloromethane were recorded on a Uvikon 930 spectrophotometer. Electro spray mass spectra were obtained in positive ion mode with a LCQ Finnigan mass spectrometer.

*4.2. General procedure for the synthesis of complexes **1**–**6***

A solution containing one equivalent of the iridium(III) precursor $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu\text{-}Cl)_2Cl_2]$ and two equivalents of imino pyridine ligand (L_1-L_6) in methanol (25 ml) was refluxed for 6 h. To the hot solution, 0.25 mmol of sodium tetraphenylborate was added. The volume was reduced to 5 ml, and the solid was precipitated using diethyl ether. The brown colored precipitate was filtered off and purified by column chromatography.

Complex **1**. (Silica gel, chloroform:methanol, 9.6:0.4), Mp: 190 °C. Yield: 85 %. IR (KBr, υ, cm^{-1}): 1594 (C = N), 1021 (py). ^1H NMR (400 MHz, CD_3CN, 25 °C):): δ (ppm) = 9.03 (br s, 1H, NH), 8.80 (dt, $^3J_{H-H}$ = 5.6 Hz, 1H, H_{ar}), 8.22–8.18 (td, $^3J_{H-H}$ = 8 Hz, 1H, H_{ar}), 8.03(d, $^3J_{H-H}$ = 8 Hz, 1H, H_{ar}), 7.82–7.79 (m, 1H, H_{ar}), 7.53–7.51(m, 2H, H_{ar}), 7.44–7.42. (m, 2H, H_{ar}), 7.32–7.29 (m, 8H, H_{ar}),7.32–7.29 (m, 1H, H_{ar}), 7.03 (t, $^3J_{H-H}$ = 7.2 Hz, 8H, H_{ar}), 6.87 (t, $^3J_{H-H}$ = 7.2 Hz, 4H, H_{ar}), 2.60 (s, 3H, H_{Me}), 1.46 (s, 15H, H_{Cp*}). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 25 °C): δ (ppm) = 153.5, 152.1, 142.0, 139.8, 135.4, 131.5, 128.1, 125.5, 125.2, 121.4, 117.0, 97.5, 15.0, 7.7. MS (ESI positive mode): *m/z* 564 $[M\text{-}BPh_4]^+$. UV–vis (10^{-4} M, CH_2Cl_2) λ_{max}(nm): 343 (ε = 2493cm^{-1} mol^{-1} L), 286 (ε = 18,734 cm^{-1} mol^{-1} L), 233 (ε = 21,077 cm^{-1} mol^{-1} L). Anal. Calcd for $C_{47}H_{48}BClN_3Ir$: C, 63.19; H, 5.42; N, 4.70. Found: C, 63.14; H, 5.40; N, 4.68.

Complex **2**. (Silica gel, chloroform:methanol, 9.5:0.5), Mp: 198 °C. Yield: 65 %. IR (KBr, υ, cm^{-1}): 1591 (C = N), 1030 (py). ^1H NMR (400 MHz, CD_3CN, 25 °C): δ (ppm) = 9.02 (br s, 1H, NH), 8.80 (dt, $^3J_{H-H}$ = 5.6 Hz, 1H, H_{ar}), 8.20 (td, $^3J_{H-H}$ = 8 Hz, 1H, H_{ar}), 8.03(d, $^3J_{H-H}$ = 8 Hz, 1H, H_{ar}), 7.83–7.79 (m, 1H, H_{ar}), 7.53–7.51 (m, 2H, H_{ar}), 7.44–7.41 (m, 2H, H_{ar}),7.32–7.28 (m, 8H, H_{ar}),7.02 (t, $^3J_{H-H}$ = 7.6 Hz, 8H, H_{ar}), 6.87 (t, $^3J_{H-H}$ = 7.2 Hz, 4H, H_{ar}), 2.6 (s, 3H, H_{Me}), 1.46 (s, 15H, H_{Cp*}). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 25 °C): δ (ppm) = 153.5, 152.1, 142.1, 139.8, 135.4, 131.5, 128.1, 125.5, 125.3, 121.4, 118.1, 97.5, 15.1, 7.8. MS (ESI positive mode): *m/z* 652 $[M\text{-}BPh_4]^+$. UV–vis (10^{-4} M, CH_2Cl_2) λ_{max} (nm): 330 (ε = 910 cm^{-1} mol^{-1} L), 276 (ε = 9906 cm^{-1} mol^{-1} L), 222 (ε = 14,407 cm^{-1} mol^{-1} L). Anal. Calcd for $C_{47}H_{47}BBrClN_3Ir$: C, 58.06; H, 4.87; N, 4.32. Found: C, 57.99; H, 4.88; N, 4.30.

Complex **3**. (Silica gel, chloroform:methanol, 9.6:0.4), Mp: 205 °C, Yield: 72 %. IR (KBr, υ, cm^{-1}): 1596 (C = N), 1030 (py). ^1H NMR (400 MHz, CD_3CN, 25 °C): δ (ppm) = 8.80 (dt, $^3J_{H-H}$ = 5.6 Hz, 1H, H_{ar}), 8.68 (br s, 1H, NH), 8.20 (td, $^3J_{H-H}$ = 8.0 Hz, 1H, H_{ar}), 8.14–8.13 (m, $^3J_{H-H}$ = 8.0 Hz, 1H, H_{ar}), 7.85–7.81 (m, 1H, H_{ar}), 7.37 (dt, $^3J_{H-H}$ = 8.0 Hz, 2H, H_{ar}), 7.33–7.28 (m, 8H, H_{ar}), 7.22 (dt, $^3J_{H-H}$ = 8.0 Hz, 2H, H_{ar}), 7.03 (t, $^3J_{H-H}$ = 7.6 Hz, 8H, H_{ar}), 6.87 (t, $^3J_{H-H}$ = 7.2 Hz, 4H, H_{ar}), 2.62 (s, 3H, H_{Me}), 1.52 (s,15H, H_{Cp*}). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 25 °C): δ (ppm) = 154.7, 151.7, 141.7, 139.8, 135.4, 129.1, 128.7, 126.7, 126.4, 125.2, 121.4, 90.2, 15.5, 7.7. MS (ESI positive mode): *m/z* 608 $[M\text{-}BPh_4]^+$. UV–vis (10^{-4} M, CH_2Cl_2) λ_{max} (nm): 333 (ε = 1360 cm^{-1} mol^{-1} L), 289 (ε = 13,908 cm^{-1} mol^{-1} L), 221 (ε = 16,270 cm^{-1} mol^{-1} L). Anal. Calcd for $C_{47}H_{47}BCl_2N_3Ir$, C, 60.84; H, 5.11; N, 4.53. Found: C, 60.86; H, 5.10; N, 4.50.

Complex **4**. (Silica gel, chloroform:methanol, 9.6:0.4), Mp: 196 °C, Yield: 70 %. IR (KBr, υ, cm^{-1}): 1597 (C = N), 1030 (py). ^1H NMR (400 MHz, CD_3CN, 25 °C): δ (ppm) = 8.84–8.82 (m, 2H, H_{ar}), 8.01 (td, $^3J_{H-H}$ = 8.0 Hz, 1H, H_{ar}), 7.82–7.79 (m, 1H, H_{ar}), 7.71–7.68 (m, 3H, H_{ar}), 7.52 (br s, 1H, NH), 7.44–7.35 (m, 5H, H_{ar}), 7.32–7.28 (m, 8H, H_{ar}), 7.26–7.24 (m, 1H, H_{ar}), 7.12 (t, $^3J_{H-H}$ = 7.6 Hz, 1H, H_{ar}), 7.03 (t, $^3J_{H-H}$ = 7.6 Hz, 8H, H_{ar}), 6.87 (t, $^3J_{H-H}$ = 7.2 Hz, 4H, H_{ar}), 1.48 (s, 15H, H_{Cp*}). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 25 °C): δ (ppm) =155.1, 151.7, 143.3, 142.7, 139.8, 135.4, 131.6, 130.2, 129.7, 128.6, 128.5, 128.4, 127.5, 127.1, 125.3, 123.0, 121.4, 117.8, 90.3, 7.4. MS (ESI positive mode): *m/z* 636 $[M\text{-}BPh_4]^+$. UV–vis (10^{-4} M, CH_2Cl_2) λ_{max} (nm): 365 (ε = 2920 cm^{-1} mol^{-1} L), 278 (ε = 21,850 cm^{-1} mol^{-1} L), 206 (ε = 35,887 cm^{-1} mol^{-1} L). Anal. Calcd for $C_{47}H_{48}BClN_3Ir$: C, 65.37; H, 5.27; N, 4.40. Found: C, 63.36; H, 5.26; N, 4.36.

Complex **5**. (Silica gel, chloroform:methanol, 9.5:0.5), Mp: 191 °C. Yield: 65 %. IR (KBr, υ, cm^{-1}): 1580 (C = N), 1031 (py). ^1H NMR (400 MHz, CD_3CN, 25 °C): δ (ppm) = 8.87 (br s, 1H, NH), 8.83 (dt, $^3J_{H-H}$ = 5.2 Hz, 1H, H_{ar}), 8.03 (td, $^3J_{H-H}$ = 8.0 Hz, 1H, H_{ar}), 7.84–7.80 (m, 1H, H_{ar}), 7.72–7.66 (m, 3H, H_{ar}), 7.50–7.34 (m, 7H, H_{ar}), 7.33–7.28 (m, 8H, H_{ar}), 7.02 (t, $^3J_{H-H}$ = 7.6 Hz, 8H, H_{ar}), 6.87 (t, $^3J_{H-H}$ = 7.2 Hz, 4H, H_{ar}), 1.51 (s, 15H, H_{Cp*}). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 25 °C): δ (ppm) = 154.9, 151.8, 142.7, 142.6, 139.9, 135.4, 131.7, 131.6, 130.2, 128.8, 128.3, 127.8, 127.3, 125.3, 121.4, 119.3, 90.5, 7.7. MS (ESI positive mode): *m/z* 714 $[M\text{-}BPh_4]^+$. UV–vis (10^{-4} M, CH_2Cl_2) λ_{max} (nm): 341 (ε = 1650 cm^{-1} mol^{-1} L), 284 (ε = 18,583 cm^{-1} mol^{-1} L), 246 (ε = 22,230 cm^{-1} mol^{-1} L). Anal. Calcd for $C_{52}H_{49}BBrClN_3Ir$: C, 60.38; H, 4.77; N, 4.06. Found: C, 60.38; H, 4.76; N, 4.06.

Complex **6** (Silica gel, chloroform:methanol, 9.6:0.4), Mp: 192 °C, Yield: 75 %. IR (KBr, υ, cm^{-1}): 1579 (C = N), 1030 (py). ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ (ppm) = 8.85 (br s, 1H, NH), 8.84–8.83 (m, 1H, H_{ar}), 8.03 (td, $^3J_{H—H}$ = 8 Hz, 1H, H_{ar}), 7.83 (td, $^3J_{H—H}$ = 8 Hz, 1H, H_{ar}), 7.73–7.34 (m, 9H, H_{ar}), 7.32–7.28 (m, 8H, H_{ar}), 7.24–7.21 (m, 1H, H_{ar}), 7.02 (t, $^3J_{H—H}$ = 7.6 Hz, 8H, H_{ar}), 6.87 (t, $^3J_{H—H}$ = 7.2 Hz, 4H, H_{ar}), 1.43 (s, 15H, H_{Cp^*}). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 25 °C): δ (ppm) = 154.9, 151.8, 142.2, 140.1, 139.9, 135.4, 131.7, 129.8, 128.8, 128.6, 128.3, 127.8, 127.7, 127.6 125.3, 121.4, 121.3, 119.1, 90.5, 7.4. MS (ESI positive mode): *m/z* 670 [M-BPh_4]$^+$. UV–vis (10^{-4} M, CH_2Cl_2) λ_{max} (nm): 373 (ε = 1369 cm^{-1} mol^{-1} L), 290 (ε = 13,790 cm^{-1} mol^{-1} L), 222 ((ε = 17,924 cm^{-1} mol^{-1} L). Anal. Calcd for $C_{47}H_{48}BClN_3Ir$: C, 63.09; H, 4.99; N, 4.24. Found: C, 63.05; H, 4.98; N, 4.25.

4.3. General procedure for the catalytic transformation of aldehydes to amides

To an oven-dried Schlenk tube, complex **3** (0.002 mmol), aldehyde (1 mmol), $NH_2OH{\cdot}HCl$ (1 mmol) and $NaHCO_3$ (1 mmol) were mixed together and the mixture was placed under an atmosphere of N_2. Dry and degassed toluene (2 ml) was added and the mixture was refluxed for the appropriate amount of time. On completion, the mixture was cooled to room temperature and the products were extracted with dichloromethane before being filtered through celite to remove the remaining unwanted components. The crude product was then extracted using silica gel chromatography (MeOH/CH_2Cl_2). The yield of the amide was determined in situ by ^{1}H NMR spectroscopy (integrations of $H_{aldehyde}$ vs H_{amide}).

4.4. Single-crystal X-ray structure analysis

Crystals of complex **3**, suitable for single-crystal X-ray structure analysis, were obtained by slow evaporation of a dichloromethane/*n*-pentane (1:1 v/v) solution. A crystal of **3** was mounted on a STOE STADIVARI Eulerian 4-circle diffractometer equipped with a Pilatus300K detector, using Cu-Kα radiation (λ = 1.54186 Å). The structure was solved and refined by direct methods using the OLEX2 platform [56]. The H-atoms were included in calculated positions and treated as riding atoms, while the non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. Crystallographic details are summarized in Table S1. Fig. 1 was drawn with Mercury [57]. A solvent void was observed in **3** and estimated to be of 155 electrons in a volume of 629.7 Å^3. This was consistent with the presence of one H_2O per asymmetric unit, which normally account for 160 electrons per unit cell. Therefore, this void was considered to be occupied by a highly disordered water molecule, and it was removed during refinement using the Mask algorithm from OLEX2.

CCDC-2368045 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336,033.

CRediT authorship contribution statement

Neelakandan Devika: Writing – original draft, Formal analysis, Data curation, Conceptualization. **Subbiah Ananthalakshmi:** Formal analysis, Data curation. **Nandhagopal Raja:** Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Gajendra Gupta:** Validation, Formal analysis, Data curation. **Bruno Therrien:** Writing – review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare no competing interests.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2024.123331.

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