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# A highly active cyclometallated iridium catalyst for the hydrogenation of iminest

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A cyclometallated iridium complex containing an imino ligand has been shown to catalyse the hydrogenation of imines. The catalyst is highly active and selective for imino bonds, with a wide variety of imines being hydrogenated in less than 1 hour at a substrate/catalyst (S/C) ratio of 2000 at 20 bar $H_2$ pressure and 75 °C.



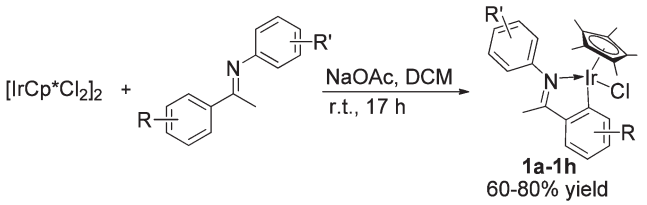
## Introduction

Amines are highly valuable compounds in both laboratory and industrial chemical syntheses. They are present in a large number of bioactive compounds, with activities of relevance to agrochemical and pharmaceutical industries.[1] Therefore, research on the production of amines has drawn a great deal of interest. Among the methods developed, hydrogenation of imines allows direct access to amines.[1–3] However, in comparison with the situation of olefins and carbonyls, catalysts that are highly efficient in imine hydrogenation are far fewer in number.[2]

Recently, a series of cyclometallated iridium-imino complexes, Iridicycles, by our group[4] and cyclometallated ruthenium, rhodium and iridium complexes by Davies[5] and de Vries[6] *et al.* were reported, which have been exploited in transfer hydrogenation reactions of imines, ketones and aldehydes and chemoselective reductive amination, including using formate as the hydrogen source in water.[2e,4c,d] We report herein that Iridicycles bearing electron-withdrawing groups are also excellent catalysts for imine reduction under hydrogenation conditions. The use of $H_2$ as the hydrogen source provides a cleaner, more scalable method.

## Results and discussion

We synthesised a range of cyclometallated iridium-imino complexes **1** by following a procedure developed by Davies *et al.* (Scheme 1).[5a] According to mechanistic studies, this acetate-assisted cyclometallation follows an electrophilic C–H activation pathway.[5c,7]




| | | | |
|---|---|---|---|
| **1a** | R: *p*-CN, R': *p*-OMe | **1e** | R: *p*-Br, R': *p*-OMe |
| **1b** | R: *p*-*i*Bu, R': *p*-OMe | **1f** | R: *p*-$NO_2$, R': *p*-OMe |
| **1c** | R: *p*-OMe, R': *p*-OMe | **1g** | R: *m*-$NO_2$, R': *p*-OMe |
| **1d** | R: H, R': *p*-OMe | **1h** | R: *p*-CN, R': H |

**Scheme 1** Synthesis of cyclometallated complexes **1**.

We started with the optimisation of the catalytic hydrogenation reaction by considering the model hydrogenation of **2a** at room temperature under 5 bar of $H_2$ (Table 1). Firstly, the activity of catalyst **1a** was compared in a series of solvents, which shows that trifluoroethanol (TFE) is the solvent of choice (Table 1, entries 1–7). It is understood that the chloride ligand needs to be dissociated in order to provide a vacant site for the coordination of $H_2$. TFE is acidic ($pK_a$ 12.5) and has high polarity and low nucleophilicity, thus facilitating the dissociation and solvation of the chloride anion, while having minimal interaction with the cationic complex.[4f,8] No reaction was observed with $[IrCp^*Cl_2]_2$ (entry 8).

One of the advantageous features of these cyclometallated complexes is the modular nature of the ligand, which allows the steric and electronic properties of the catalyst to be fine-tuned with ease. The electronic effect of the substituents in the ligand was subsequently studied (entries 9–16). The electron-deficient group at the *para*-position of the ketone ring clearly enhances the catalytic activity (entries 9 and 13–14). The position of the substituent has a significant effect on the catalyst as well, as a $NO_2$ group at the *meta*-position led to a much lower conversion (entry 14 *vs.* 15). The *para*-MeO group at the aniline ring also proves to be critical (entry 9 *vs.* 16). The

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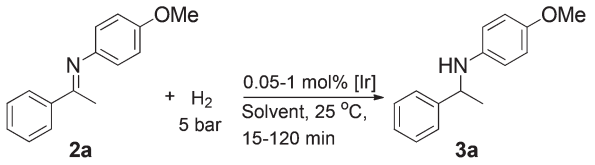
†Electronic supplementary information (ESI) available: ESI features detailed analytic data of catalysts and all products. See DOI: 10.1039/c3ob41150h

**Table 1** Optimisation of the hydrogenation of **2a**[a]




**2a** **3a**

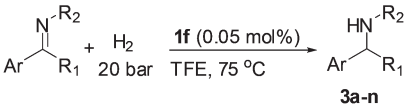
| Entry | [Ir] | mol% [Ir] | Solvent | *t* (min) | Conv.[b] (%) |
|---|---|---|---|---|---|
| 1 | **1a** | 1 | DMSO | 120 | N.R. |
| 2 | **1a** | 1 | DMF | 120 | N.R. |
| 3 | **1a** | 1 | DCM | 120 | N.R. |
| 4 | **1a** | 1 | Toluene | 120 | N.R. |
| 5 | **1a** | 1 | MeOH | 120 | 7 |
| 6 | **1a** | 1 | EtOH | 120 | 2 |
| 7 | **1a** | 1 | TFE | 120 | >99 |
| 8 | $[IrCp^*Cl_2]_2$ | 0.2 | TFE | 30 | 1 |
| 9 | **1a** | 0.2 | TFE | 30 | 74 |
| 10 | **1b** | 0.2 | TFE | 30 | 9 |
| 11 | **1c** | 0.2 | TFE | 30 | 21 |
| 12 | **1d** | 0.2 | TFE | 30 | 51 |
| 13 | **1e** | 0.2 | TFE | 30 | 54 |
| 14 | **1f** | 0.2 | TFE | 30 | 87 |
| 15 | **1g** | 0.2 | TFE | 30 | 26 |
| 16 | **1h** | 0.2 | TFE | 30 | 37 |
| 17 | **1f** | 0.2 | TFE | 15 | 76 |
| 18[c] | **1f** | 0.2 | TFE | 15 | 95 |
| ***19***[d] | ***1f*** | ***0.05*** | ***TFE*** | ***30*** | ***>99*** |

[a] Reaction conditions: 1 mmol of **2a**, complex **1** (0.05–1 mol%), solvent (1.5 mL), 5 bar of $H_2$ and 25 °C unless otherwise indicated, 15–120 min. [b] Conversion was determined by $^1H$ NMR of the crude reaction mixture; N.R. = no reaction. [c] 20 bar of $H_2$. [d] 20 bar of $H_2$, 75 °C.

best result was obtained with complex **1f**. Having identified the most active catalyst, our attention turned to optimization of other parameters. The increase of the hydrogen pressure had a positive effect on the catalytic activity (entry 18). An increase in temperature also led to higher activity, allowing for almost complete hydrogenation of **2a** in 30 min with only 0.05 mol% of **1f** (entry 19). With these results in hand, the optimal conditions chosen for investigating the substrate scope were set at 20 bar of hydrogen, 75 °C and a low catalyst loading of 0.05 mol%.

A series of imine substrates were hydrogenated to demonstrate the high activity and versatility of this Iridicycle catalyst. At an S/C ratio of 2000 a wide range of imines were efficiently hydrogenated, with reaction times ranging from 5 to 75 minutes. Table 2 presents the results of the hydrogenation of imines derived from aromatic ketones and an aldehyde. The catalyst tolerates functional groups with different electronic properties on the ketone (entries 1–7), albeit requiring longer reaction times for electron-deficient ketimines. The catalyst also tolerates *meta*- (entry 7), di- (entry 6) or even more sterically demanding *ortho*-substitution (entry 8). In this regard, it is worth noting that the catalyst is effective for the synthesis of sterically relatively hindered amines (entry 9). A cyclic imine was also hydrogenated (entry 10). Aldimines are particularly active under the conditions developed. Thus, even at an S/C of

**Table 2** Hydrogenation of imines derived from aromatic ketones/aldehydes with **1f**[a]




**3a-n**

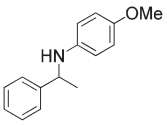
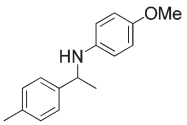
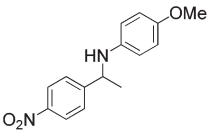
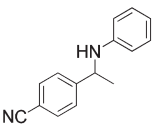
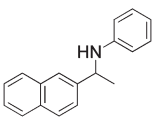
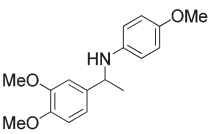
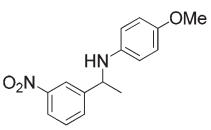
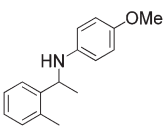
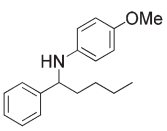
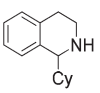
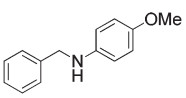
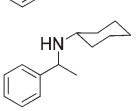
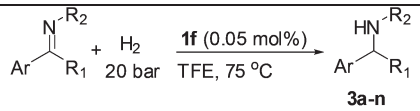
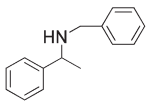
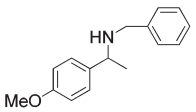
| Entry | Product | *t* (min) | Yield[b] (%) |
|---|---|---|---|
| 1 |  | 30 | 92 |
| 2 |  | 30 | 85 |
| 3 |  | 60 | 89 |
| 4 |  | 75 | 89 |
| 5 |  | 45 | 87 |
| 6 |  | 60 | 92 |
| 7 |  | 60 | 91 |
| 8 |  | 45 | 92 |
| 9 |  | 60 | 93 |
| 10 |  | 120 | 95 |
| 11[c] |  | 5 | 91 |
| 12 |  | 60 | 78 |

**Table 2** *(Contd.)*




3a-n

| Entry | Product | *t* (min) | Yield[b] (%) |
|---|---|---|---|
| 13 |  | 75 | 81 |
| 14 |  | 90 | 85 |

[a] Reaction conditions: 1 mmol of imine, 0.05 mol% **1f**, 1.5 mL TFE, 20 bar of $H_2$, 75 °C, 5–120 minutes. [b] Isolated yields. [c] 0.025 mol% **1f**.

4000, amine **3k** was isolated in 91% yield after only 5 minutes (entry 11), resulting in a high TOF of $4.4 \times 10^4$ $h^{-1}$.

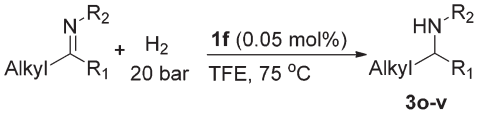
This catalyst is also effective for the hydrogenation of *N*-benzyl imines (Table 2, entries 13 and 14). The corresponding amines can then be easily debenzylated by hydrogenolysis with Pd/C, providing a simple route for the synthesis of primary amines. The catalyst is chemoselective of C=N bonds over the benzyl group.

Table 3 summarises the results of the hydrogenation of imines derived from aliphatic ketones and aldehyde. Lower yields than those in Table 2 were recorded, probably due to the low stability of the aliphatic ketimines. Indeed, free aniline was detected by NMR in the crude products of some of these reactions. The catalyst tolerates electron-donating and -withdrawing groups in the aniline ring (entries 1–4) as well as sterically hindered anilines (entries 2 and 4). The excellent chemoselectivity exhibited by the catalyst is worth noting. Thus, C=N double bonds were reduced selectively in the presence of other reducible groups, such as internal and external alkenes (entries 5 and 6, respectively). No reduction of the C=C double bond was observed in the $^1$H NMR spectrum of the crude product.

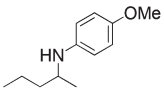
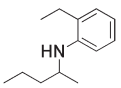
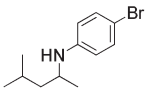
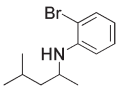
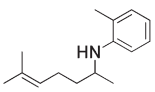
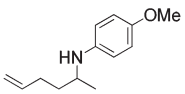
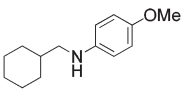
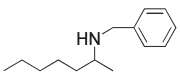
Preliminary mechanistic studies were undertaken in order to gain some insight into the catalytic cycle. As mentioned before, the hydrogenation benefits from higher $H_2$ pressure. Fig. 1 shows that there is almost a linear correlation between the conversion and $H_2$ pressure, indicating that $H_2$ is probably involved in the rate-determining step of the hydrogenation.

The effect of the concentration of the imine substrate and catalyst on the initial reaction rate has also been examined. As shown in Fig. 2, there is negligible variation of the rate when the concentration of the substrate increases (▲). This suggests that the reaction rate is zero order with respect to the imine substrate. On the other hand, there is almost a linear dependence of the initial rate on the concentration of the catalyst (■). These results rule out the possibility of hydride transfer controlling the catalytic turnover and suggest that the imine

**Table 3** Hydrogenation of imines derived from aliphatic ketones/aldehydes[a]




3o-v

| Entry | Product | *t* (min) | Yield[b] (%) |
|---|---|---|---|
| 1 |  | 30 | 79 |
| 2 |  | 30 | 71 |
| 3 |  | 40 | 71 |
| 4 |  | 30 | 81 |
| 5 |  | 20 | 67 |
| 6 |  | 30 | 48 |
| 7[c] |  | 5 | 82 |
| 8 |  | 60 | 73 |

[a] The reaction conditions were the same as those in Table 2. [b] Isolated yields. [c] 0.025 mol% **1f**.

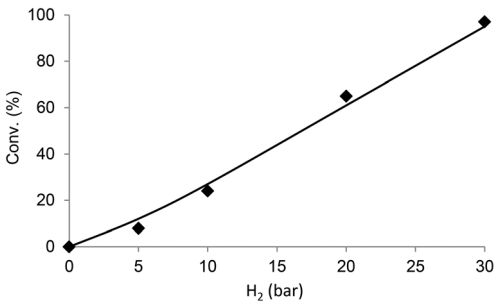



**Fig. 1** Effect of $H_2$ pressure on the conversion of **2a**. Reaction conditions: 1 mmol of **2a**, 0.2 mol% of **1f**, 1.5 mL TFE, $H_2$, 25 °C for 5 min. The conversion was determined by $^1$H NMR.

hydrogenation in question is probably rate-limited by the step of hydride formation. Fig. 2 also reveals that little hydrogenation takes place when the catalyst concentration is very low (<0.17 mM). This presumably results from the catalyst being poisoned by a small amount of impurities, *e.g.* $O_2$, present in the hydrogen gas or the system. The iridium-hydride intermediate may be sensitive to oxygen.[9]

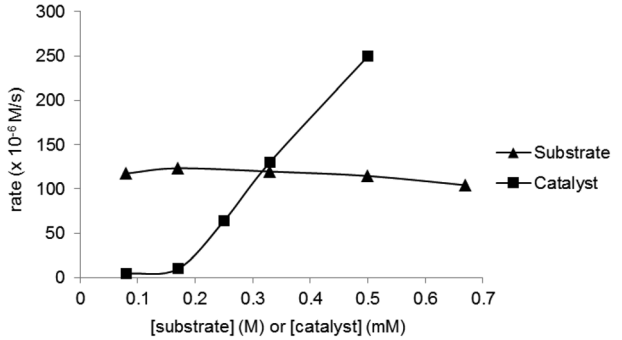
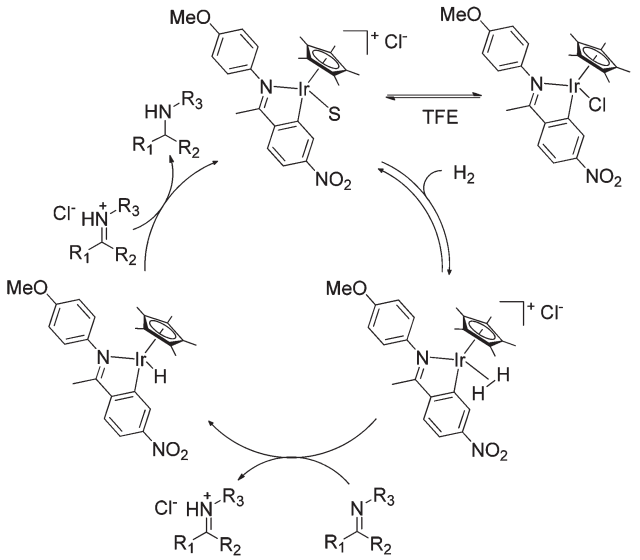



**Fig. 2** Effect of the substrate and catalyst concentrations on the initial reaction rate of hydrogenation of **2a**. Initial rates were calculated using conversions (<10%) and based on the average of 3 reactions. Reaction conditions: 1.5 mL of TFE at 25 °C, 5 bar of $H_2$; 0.33 mM of catalyst for (▲); 0.17 M substrate for (■).




**Scheme 2** Proposed catalytic cycle for the ionic hydrogenation of imines (S may be a substrate molecule).

We propose that catalyst **1f** promotes hydrogenation through an ionic pathway which involves no imine coordination (Scheme 2).[10,11] Following dissociation of the chloride from **1f**, which is likely to be promoted by TFE, the catalytic cycle is made up of 3 steps: reversible coordination of $H_2$, turnover-limiting heterolytic cleavage of $H_2$ into a hydride and a proton to be taken up by the imine, and subsequent transfer of the hydride to the resulting iminium cation. Mechanistic studies on the ionic pathway and the hydrogenation of imines have been reported previously.[12]

## Conclusions

Cyclometallated iridium complexes have been shown to be highly active and chemoselective for the reduction of imines under hydrogenation conditions. The combination of air-stability and ease of synthesis of catalysts and a simple work-up procedure for the hydrogenation makes the Iridicycles attractive for academic and industrial applications. Evidence suggests that the hydrogenation is probably turnover-limited by the step of hydride formation.

## Experimental

### General

Unless otherwise specified, all reagents were obtained commercially and used without further purification. $CH_2Cl_2$ was dried over $CaH_2$ and distilled prior to use. $^1H$ and $^{13}C$ NMR spectra were recorded at 400 ($^1H$) and 100 ($^{13}C$) MHz in ppm with reference to TMS as an internal standard in $CDCl_3$ at ambient temperature unless otherwise stated. Mass spectra were obtained by chemical ionization (CI). All compounds were characterised by $^1H$ and $^{13}C$ NMR, MS, HRMS and microanalysis. Analytic data for new iridium complexes are given below. Imines were prepared according to a literature procedure.[11]

### General procedure for the synthesis of cyclometallated complexes[4,5]

An oven-dried Schlenk tube containing a stir bar was charged with $[IrCp^*Cl_2]_2$ (1 eq.), imine ligand (2 eq.) and NaOAc (10 eq.). Following degassing with $N_2$ three times, freshly distilled $CH_2Cl_2$ was then injected. The resulting mixture was stirred at rt overnight. The reaction mixture was then filtered through celite and concentrated *in vacuo*. The resulting solid was washed with diethyl ether/hexane.

### Typical procedure for imine hydrogenation with cyclometallated iridium complexes

A glass liner containing a stir bar was charged with an imine (1 mmol) and TFE was added (0.5 mL, except for the synthesis of **3k** and **3u** where 1 mL was used). The mixture was stirred until the imine was dissolved. 1 mL (0.5 mL for the products **3k** and **3u**) of a stock solution (5 mM) containing the catalyst **1f** was then added. The glass liner was then placed in an autoclave followed by degassing with $H_2$ three times. The hydrogenation was carried out at 20 bar of $H_2$ with stirring at 75 °C for 5–120 min. The stirring was then stopped and the autoclave allowed to cool down to rt. The hydrogen gas was then carefully released in the fumehood and the solution transferred to a flask and concentrated *in vacuo* to afford the crude product. Flash chromatography purification with a column of silica gel eluted with petroleum ether–ethyl acetate (20 : 1 to 5 : 1) yielded the desired amine product.

**Iridium complex 1b.** The product was obtained as a bright yellow solid according to the cyclometallation procedure in 17 h; $^1H$ NMR (400 MHz, 253 K, $CDCl_3$) $\delta$ 0.94 (d, $J$ = 6.7 Hz, 3H), 0.97 (d, $J$ = 6.5 Hz, 3H), 1.43 (s, 15H), 1.91–1.98 (m, 1H), 2.43 (s, 3H), 2.57–2.57 (m, 2H), 3.87 (s, 3H), 6.79 (d, $J$ = 5.4 Hz, 1H), 6.84 (d, $J$ = 7.5 Hz, 1H), 6.89 (d, $J$ = 5.4 Hz, 1H), 6.98 (d, $J$ = 6.7 Hz, 1H), 7.45 (d, $J$ = 7.5 Hz, 1H), 7.60 (s, 1H), 7.80 (d, $J$ = 6.7 Hz, 1H); $^{13}C$ NMR (100 MHz, 253 K, $CDCl_3$) $\delta$ 8.8, 17.1,

22.7, 23.0, 30.8, 46.1, 55.6, 88.9, 112.2, 114.8, 122.8, 123.5, 125.0, 128.3, 136.0, 144.2, 145.5, 146.0, 157.3, 167.7, 181.2; Anal Calcd for $C_{29}H_{37}ClIrNO$: C, 54.15; H, 5.80; N, 2.18. Found: C, 54.66; H, 5.90; N, 2.06.

**Iridium complex 1e.** The product was obtained as a bright orange solid according to the cyclometallation procedure in 17 h; $^1$H NMR (400 MHz, 253 K, $CDCl_3$) $\delta$ 1.43 (s, 15H), 2.43 (s, 3H), 3.88 (s, 3H), 6.82 (d, $J$ = 8.4 Hz, 1H), 6.91 (d, $J$ = 8.4 Hz, 1H), 7.00 (d, $J$ = 8.3 Hz, 1H), 7.18 (dd, $J$ = 8.2, 1.8 Hz, 1H), 7.39 (d, $J$ = 8.3 Hz, 1H), 7.79 (d, $J$ = 8.2 Hz, 1H), 7.91 (d, $J$ = 1.8 Hz, 1H); $^{13}$C NMR (100 MHz, 253 K, $CDCl_3$) $\delta$ 8.7, 17.3, 55.6, 89.4, 112.3, 114.9, 124.5, 127.5, 130.0, 137.2, 143.8, 145.1, 146.5, 152.6, 157.6, 170.1, 180.9; Anal Calcd for $C_{25}H_{28}BrIrNO$: C, 45.08; H, 4.24; N, 2.10. Found: C, 44.98; H, 4.25; N, 2.02.

**Iridium complex 1f.** The product was obtained as a black solid according to the cyclometallation procedure in 17 h; $^1$H NMR (400 MHz, 253 K, $CDCl_3$) $\delta$ 1.46 (s, 15H), 2.52 (s, 3H), 3.89 (s, 3H), 6.84–6.86 (m, 1H), 6.94–6.96 (m, 1H), 7.03 (d, $J$ = 8.6 Hz, 1H), 7.64 (d, $J$ = 8.5 Hz, 1H), 7.79 (d, $J$ = 7.8 Hz, 1H), 7.89 (dd, $J$ = 8.5, 2.2 Hz, 1H), 8.63 (d, $J$ = 2.2 Hz, 1H); $^{13}$C NMR (100 MHz, 253 K, $CDCl_3$) $\delta$ 8.81, 55.7, 90.1, 112.5, 115.1, 117.1, 123.1, 124.4, 128.7, 129.2, 143.6, 148.8, 153.5, 157.9, 168.4, 180.5; HRMS for $C_{25}H_{28}ClIrN_2NaO_3$ $[M + Na]^+$: $m/z$ Calcd: 653.1292; Found: 653.1268; Anal Calcd for $C_{25}H_{15}ClIrN_2O_3$: C, 47.50; H, 4.46; N, 4.43. Found: C, 47.94; H, 4.51; N, 4.40.

**Iridium complex 1g.** The product was obtained as a red solid according to the cyclometallation procedure in 17 h. It is a mixture of two regioisomers in a ratio of 7 : 1, with the major regioisomer having the $NO_2$ group *para* to the iridium; $^1$H NMR (400 MHz, 253 K, $CDCl_3$) $\delta$ 1.41 (s, 1.9H), 1.44 (s, 13.1H), 2.35 (s, 0.4H), 2.55 (s, 2.6H), 3.86 (s, 0.4H), 3.88 (s, 2.6H), 6.80 (d, $J$ = 8.6 Hz, 0.3H), 6.85 (d, $J$ = 8.0 Hz, 0.8H), 6.95 (d, $J$ = 8.8 Hz, 1.2H), 7.02 (d, $J$ = 8.2 Hz, 0.8H), 7.66 (t, $J$ = 8.0 Hz, 0.2H), 7.72 (d, $J$ = 8.0 Hz, 0.8H), 7.96 (d, $J$ = 8.4 Hz, 0.8H), 8.06 (dd, $J$ = 8.4, 1.5 Hz, 0.8H), 8.35 (d, $J$ = 1.5 Hz, 1H), 8.82 (s, 0.1H); $^{13}$C NMR (100 MHz, 253 K, $CDCl_3$) $\delta$ 8.8 (M), 9.0 (m), 17.4 (M), 17.7 (m), 55.6 (m), 55.7 (M), 90.2 (m), 90.6 (M), 112.5, 114.2, 115.2, 121.0, 122.2, 123.2, 123.3, 124.4, 125.1, 126.0, 129.6, 133.2, 135.7, 141.1, 142.7, 143.3, 143.5, 148.1, 148.6, 156.2, 157.9, 163.7, 173.9, 180.8, 181.1, 181.9; Anal Calcd for $C_{25}H_{15}ClIrN_2O_3$: C, 47.50; H, 4.46; N, 4.43. Found: C, 47.44; H, 4.37; N, 4.41.

**Iridium complex 1h.** The product was obtained as a deep red solid according to the cyclometallation procedure in 17 h; $^1$H NMR (400 MHz, 253 K, $CDCl_3$) $\delta$ 1.42 (s, 15H), 2.49 (s, 3H), 6.88 (d, $J$ = 7.6 Hz, 1H), 7.27–7.31 (m, 1H), 7.35 (d, $J$ = 8.0 Hz, 1H), 7.45 (t, $J$ = 7.6 Hz, 1H), 7.52 (t, $J$ = 7.6 Hz, 1H), 7.59 (d, $J$ = 8.0 Hz, 1H), 7.80 (d, $J$ = 7.6 Hz, 1H), 8.06 (s, 1H); $^{13}$C NMR (100 MHz, 253 K, $CDCl_3$) $\delta$ 3.9, 12.8, 85.2, 109.6, 115.3, 117.3, 118.3, 120.5, 122.2, 123.2, 123.6, 125.6, 133.6, 145.4, 146.9, 162.9, 176.1; Anal Calcd for $C_{25}H_{26}ClIrN_2$: C, 51.58; H, 4.50; N, 4.81. Found: C, 51.58; H, 4.44; N, 4.64.

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