

# Heterobimetallic Cu(I)–Rh(I) and Cu(I)–Ir(I) Complexes: Synthesis, Catalytic Applications in Transfer Hydrogenation, and Photophysical Properties

Shubham, Vanitha R. Naina, Mohd Iqbal, Michael T. Gamer, and Peter W. Roesky\*

The syntheses and structural characterization of Cu(I)–Rh(I) and Cu(I)–Ir(I) complexes are reported. These complexes are synthesized via the reaction of a previously reported copper amidinate complex,  $\text{Cu}_2\text{L}_2$  ( $\text{L} = \{\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})_2\}$ ,  $\text{Dipp} = N,N'$ -2,6-diisopropylphenyl), with  $[\text{M}(\text{cod})\text{Cl}]_2$  ( $\text{M} = \text{Rh}, \text{Ir}$ ;  $\text{cod} = 1,5$ -cyclooctadiene) yielding complexes  $[\{(\text{M}(\text{cod})\text{Cl})\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})_2\}_2\text{Cu}_2]$  ( $\text{M} = \text{Rh}, \text{Ir}$ ). Additionally, an alternative one-pot synthetic route is explored by the reaction of lithium salt of the ligand,  $[\text{M}(\text{cod})\text{Cl}]_2$  ( $\text{M} = \text{Rh}, \text{Ir}$ ), and  $\text{CuCl}$ , resulting in improved yields of  $[\{(\text{M}(\text{cod})\text{Cl})\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})_2\}_2\text{Cu}_2]$ . Further, reaction of lithium salt of the ligand with  $[\text{M}(\text{cod})\text{Cl}]_2$  ( $\text{M} = \text{Rh}, \text{Ir}$ ) leads to the formation of intermediate complexes  $[\{(\text{M}(\text{cod})\text{Cl})\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})_2\}\text{Li}(\text{thf})_3]$  ( $\text{M} = \text{Rh}, \text{Ir}$ ), which upon hydrolysis,

yielded protonated amidinate derivatives  $[(\text{M}(\text{cod})\text{Cl})\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})(\text{NHDipp})]$  ( $\text{M} = \text{Rh}, \text{Ir}$ ). In the second pathway, lithium salt of the ligand is hydrolyzed to obtain  $[\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})(\text{NHDipp})]_2$  and further reaction with  $[\text{M}(\text{cod})\text{Cl}]_2$  ( $\text{M} = \text{Rh}, \text{Ir}$ ) yields  $[(\text{M}(\text{cod})\text{Cl})\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})(\text{NHDipp})]$  via an alternative reaction pathway. The catalytic potential of Cu(I)–Ir(I) complex  $[\{(\text{Ir}(\text{cod})\text{Cl})\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})_2\}_2\text{Cu}_2]$  is evaluated for transfer hydrogenation (TH) of aryl aldehydes using isopropanol as a hydrogen transfer source. Furthermore, the Ir complexes  $[\{(\text{Ir}(\text{cod})\text{Cl})\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})_2\}_2\text{Cu}_2]$  and  $[(\text{Ir}(\text{cod})\text{Cl})\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})(\text{NHDipp})]$  are found to be luminescent in the solid state at 77 K with an emission maximum around 580 nm.

## 1. Introduction

Heterobimetallic complexes are of great interest because of their applications in optoelectronics,<sup>[1]</sup> catalysis,<sup>[2,3]</sup> molecular magnetism,<sup>[4,5]</sup> and medical applications.<sup>[6,7]</sup> These complexes can consist of different metals bridged by an orthogonal ligand<sup>[8–10]</sup> or direct metal–metal interactions.<sup>[11,12]</sup> In the orthogonal ligand systems, different affinities of the metal atoms to different segments of the ligand can be harvested, which are due to “hard and soft acids and bases” (HSAB) interactions.<sup>[13–15]</sup>

Several examples of Cu(I) heterobimetallic complexes incorporating other transition metals have been successfully synthesized using the orthogonal ligand systems following the same HSAB principle.<sup>[16–19]</sup> Focusing on the copper amidinate complexes, it is observed that most of them predominantly exist in the form of a planar dimer bridged by linear N–Cu–N bonding

units.<sup>[20–23]</sup> The dimeric network of the type  $\text{Cu}_2\text{L}_2$  ( $\text{L} = \text{amidinate ligand}$ ) is supported by the weak yet significant cuprophilic interactions,<sup>[24–28]</sup> which are the inherent property of  $d^{10}$  metals and play a crucial role in maintaining the structural integrity and electronic properties of these complexes.<sup>[29–33]</sup>

Heterobimetallic complexes of transition metals provide the benefit of tandem catalysis by combining multiple catalytic cycles in a sequential manner, and they offer several advantages, like saving time, reducing waste, and enhancing overall efficiency in organic synthesis.<sup>[34–37]</sup> This approach has proven to be highly effective in chemical reactions and generating the products with high selectivity and yield.<sup>[38–41]</sup> A few examples of copper-containing heterobimetallic complexes have been used in many catalytic reactions such as hydroboration, alkynylation, reduction of  $\text{CO}_2$  to ethanol, oxidation of alcohols, etc.<sup>[42–45]</sup>

Alcohols have a number of applications in organic syntheses,<sup>[46,47]</sup> pharmaceutical industries,<sup>[48]</sup> and agrochemical industries.<sup>[49]</sup> Aldehydes and ketones can be transformed into alcohols using the stoichiometric amount of reagents like  $\text{NaBH}_4$ ,  $\text{LiAlH}_4$ , etc.,<sup>[50,51]</sup> or using molecular hydrogen by the process of catalytic hydrogenation.<sup>[52]</sup> Instead of using these reagents in quantitative amounts, catalytic processes provide an alternative for such conversions.<sup>[53]</sup> Transfer hydrogenation (TH) is one of the catalytic processes that fulfills this requirement. There have been a lot of examples of the transition metal complexes based on Co, Ni, Ru, Rh, Pd, and Ir, which are capable of TH catalysis using formic acid, isopropanol, methanol, ethanol, or dihydroanthracene as hydrogen donor sources.<sup>[54–60]</sup>

Some of the selected examples of iridium complexes coordinated by phosphines are depicted in **Figure 1**, which have been

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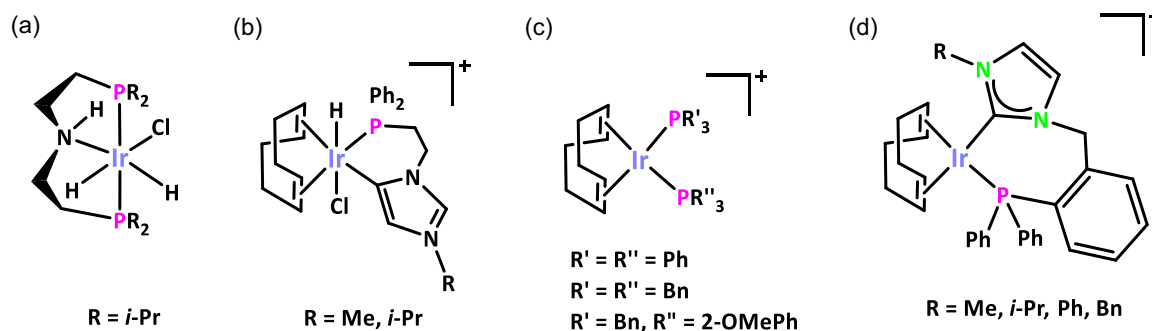


Figure 1. Selected examples of Ir(III) a,b) and Ir(I) complexes c,d) used for TH catalysis.

used for the TH. The first two examples (Figure 1a and b) have an Ir(III) center and the other two (c and d) have an Ir(I) center as the active site. In 2006, air stable iridium chlorodihydride complex bearing phosphine ligands (Figure 1a) was used as a catalyst for TH of ketones in isopropanol.<sup>[61]</sup> Later in 2011, Ir(III) complexes bearing abnormal *N*-heterocyclic carbenes (NHCs) and phosphine (Figure 1b) were observed to be active catalysts for TH of ketones or enones, dehydrative C–C coupling between primary and secondary alcohols and dehydrogenation of benzyl alcohol to benzyl benzoate.<sup>[62]</sup> Lugo et al. used Ir(I) cationic complexes for a similar purpose of TH of ketones (Figure 1c).<sup>[63]</sup> Most of the TH reactions require high temperature or pressure and a base additive, but in 2020, Andersson et al. reported cationic NHC-phosphine Ir(I) complexes (Figure 1d) for the same objective under ambient conditions without the addition of a base.<sup>[64]</sup>

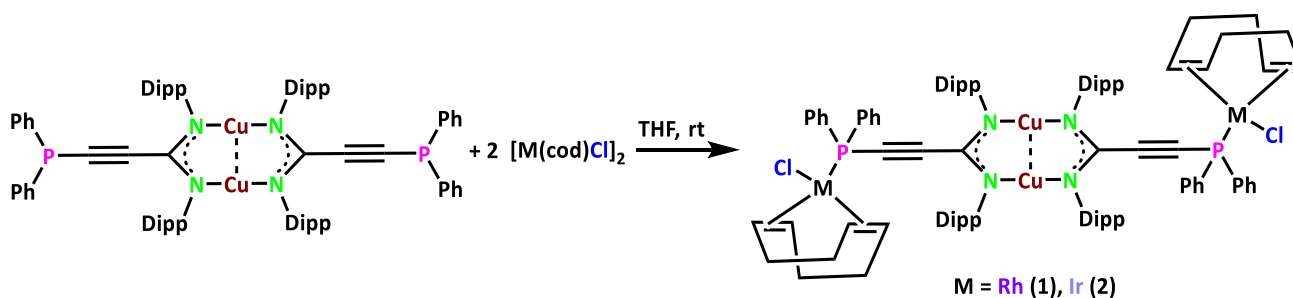
Herein, we describe the synthesis of Cu(I)–Rh(I) and Cu(I)–Ir(I) heterobimetallic complexes stabilized by the phosphine-substituted acetylide amidinate ligand. We outlined the synthetic route in a step-wise manner, starting with the synthesis of Cu(I), Rh(I), and Ir(I) complexes, as well as demonstrating a one-pot synthesis method. Additionally, Rh(I) and Ir(I) complexes with the protonated ligand were isolated. Furthermore, Cu(I)–Ir(I) complex was employed as a catalyst for the catalytic hydrogen transfer to the aryl aldehydes. The Ir(I) and Cu(I)–Ir(I) complexes were found to be luminescent in the solid state and in dichloromethane solution at 77 K and studied for their photophysical properties.

## 2. Results and Discussion

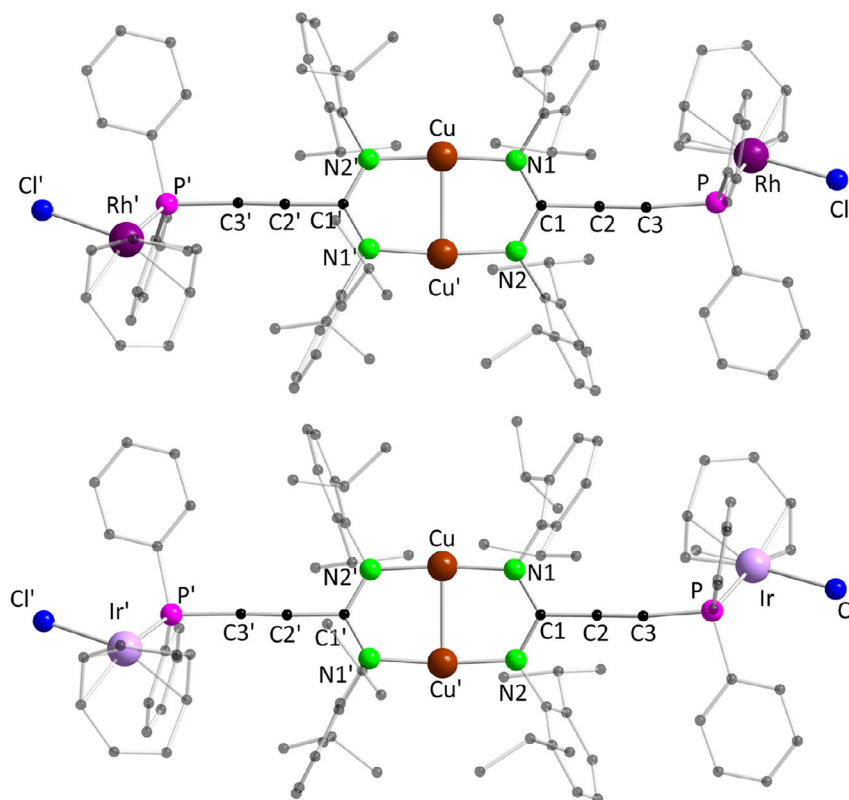
### 2.1. Syntheses and Characterization

The synthesis of heterobimetallic complexes **1** and **2** was accomplished by the overnight reaction of previously reported copper amidinate complex  $[\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})_2]_2\text{Cu}_2$  ( $\text{Cu}_2\text{L}_2$ ; Dipp = *N,N'*-2,6-diisopropylphenyl),<sup>[10]</sup> a metalloligand, with one equivalent of the  $[\text{Rh}(\text{cod})\text{Cl}]_2$  and  $[\text{Ir}(\text{cod})\text{Cl}]_2$  (cod = 1,5-cyclooctadiene), respectively, in tetrahydrofuran (THF) under ambient conditions (Scheme 1). After workup,  $[\{\text{Rh}(\text{cod})\text{Cl}\}\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})_2]_2\text{Cu}_2$  (**1**) was obtained as a yellow colored solid in a 79% yield, while  $[\{\text{Ir}(\text{cod})\text{Cl}\}\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})_2]_2\text{Cu}_2$  (**2**) was amber colored with a 74% yield.

Compounds **1** and **2** were thoroughly characterized by single-crystal X-ray diffraction (SC-XRD) (Figure 2), nuclear magnetic resonance (NMR), and infrared (IR) spectroscopy, as well as elemental analysis (EA). Both the complexes were found to be structurally similar to each other and they crystallized in the triclinic space group  $P\bar{1}$  (Figure 2). The Rh and Ir centers were coordinated by the phosphine from the metalloligand and the cod ligand, in addition to a chloride ion. The Cu–Cu bond length in the central  $\text{Cu}_2\text{L}_2$  unit was observed to be 2.462(10) Å and 2.465(6) Å in **1** and **2**, respectively, which are in a good agreement with the reported cuprophilic interactions, confirming the presence of significant Cu–Cu interactions within the structures.<sup>[24]</sup> In both the complexes, N–Cu–N units exhibit almost linear geometry with a bond angle of  $\approx 175^\circ$  closely resembling the geometries observed



Scheme 1. Synthesis of heterobimetallic Cu(I)–Rh(I) (**1**) and Cu(I)–Ir(I) (**2**) complexes from Cu(I) metalloligand  $[\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})_2]_2\text{Cu}_2$ .



**Figure 2.** Molecular structure of **1** (top) and **2** (bottom) in the solid state. Hydrogen atoms and noncoordinating solvent molecules are omitted for clarity. Thermal ellipsoid representations and structural parameters are given in the ESI (Figures S38 and S39, Supporting Information).

for previously reported Cu(I)—Au(I) systems.<sup>[10]</sup> The Rh—P and Ir—P bond distances were found to be 2.293(2) Å and 2.284(9) Å, respectively, which were nearly similar to each other and consistent with previously reported values for related complexes.<sup>[65–68]</sup> The P—Rh—Cl and P—Ir—Cl bond angles were found to be closer to the right angle, 91.3(6)° and 92.2(3)°, respectively.

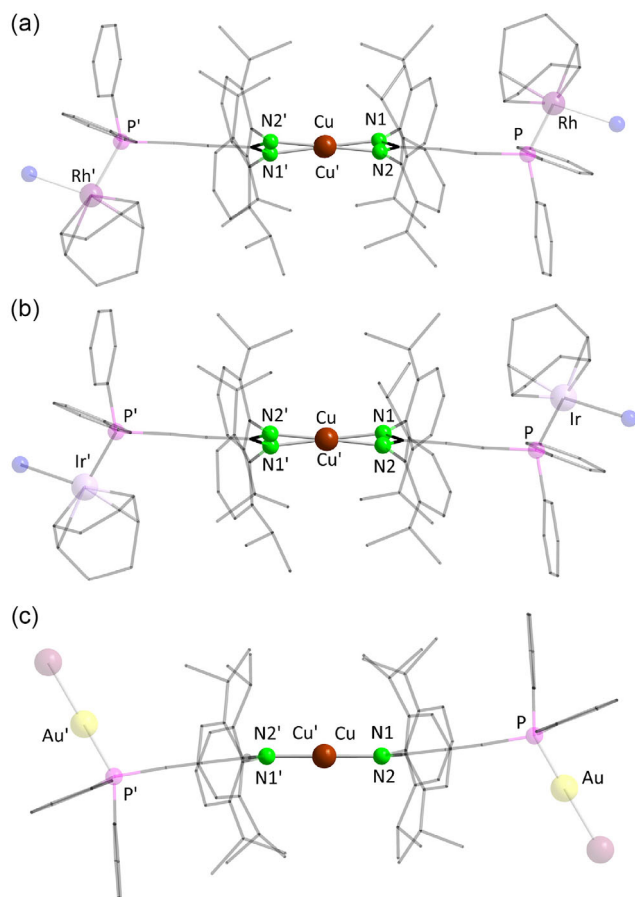
The structural analysis of **1** and **2** also led us to the significant finding about the eight-membered ring, containing two Cu atoms, two carbon atoms, and four nitrogen atoms of the amidinate ligand. The key observation was that this ring adopts a nonplanar conformation, in contrast to the previously reported complex  $[(\text{Au})\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})_2]_2\text{Cu}_2$ , which exhibits an entirely planar arrangement with a torsional angle of precisely 0° (Figure 3c).<sup>[10]</sup> In the case of complex **1**, the torsional angle defined by the N1—N2—N1'—N2' atoms was measured to be 19.7° (Figure 3a), indicating a deviation from planarity. Similarly, complex **2** exhibits a comparable nonplanarity, with a slightly lower torsional angle of 19.5° (Figure 3b). These findings highlight the structural distinctions between these complexes and the influence of the type of metal coordinated at the phosphine center.

The <sup>1</sup>H NMR spectra suggest that the structures have been retained in the solution as well containing the characteristic signals. The observed signals for Cu<sub>2</sub>L<sub>2</sub> unit are similar to the reported ones, e.g.,  $[(\text{AuX})\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})_2]_2\text{Cu}_2$  (X = Cl, Br, I and Mes),<sup>[10]</sup> with a slight shift and are observed at  $\delta = 3.28$

and 3.32 ppm as a heptet for isopropyl arm of **1** and **2**, respectively, and two sets of doublets near  $\delta = 1.00$  ppm for the methyl arms of Dipp moiety. Additionally, three sets of signals were observed at  $\delta = 2.75$ , 2.27–2.06, and 1.98–1.78 ppm for **1** and at  $\delta = 2.33$ , 2.11–1.88, and 1.82–1.45 ppm for **2**, which can be attributed to cod protons. Moreover, a doublet at  $\delta = 12.3$  ppm was obtained in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **1** with a coupling constant of <sup>1</sup>J<sub>P–Rh</sub> = 158.5 Hz, whereas a singlet was obtained at  $\delta = 4.1$  ppm for complex **2**.

Furthermore, the reaction of two equivalents of phosphine-substituted lithium acetylide amidinate was performed with one equivalent of [Rh(cod)Cl]<sub>2</sub> and [Ir(cod)Cl]<sub>2</sub> in THF under ambient conditions for 12 h to obtain complexes **3** and **4**, respectively, in quantitative yields (Scheme 2). Unfortunately, we were not able to crystallize and fully characterize complexes **3** and **4**, so, we proceeded with their hydrolysis to get the corresponding complexes **6** and **7**, respectively, with protonated amidinates (Scheme 2). Complexes **6** and **7** were crystallized by layering pentane over the saturated solution of toluene. The complexes **6** and **7** were also obtained from an alternative route by the reaction of protonated amidinate ligand [Ph<sub>2</sub>PC≡CC(NDipp)(NHDipp)]<sub>2</sub> (**5**) with [Rh(cod)Cl]<sub>2</sub> and [Ir(cod)Cl]<sub>2</sub>, respectively. For this, **5** was prepared by the hydrolysis of lithium salt of the ligand (Scheme 2) and was crystallized in a concentrated THF solution.

Structurally, the bonding situation of complexes **6** and **7** was almost similar to complexes **1** and **2**, except the absence of Cu(I)

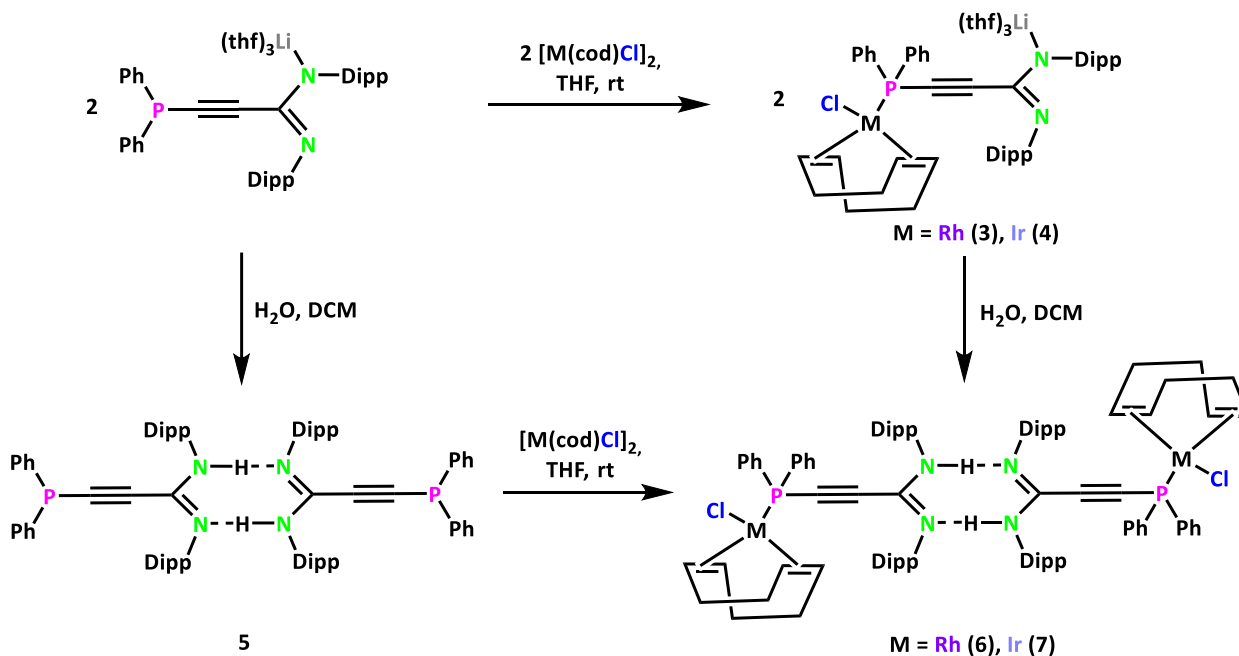


**Figure 3.** Comparison of the torsional angle of 1 a) top and 2 b) center with  $[(\text{Au})\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})_2]_2\text{Cu}_2$  complex c) bottom.

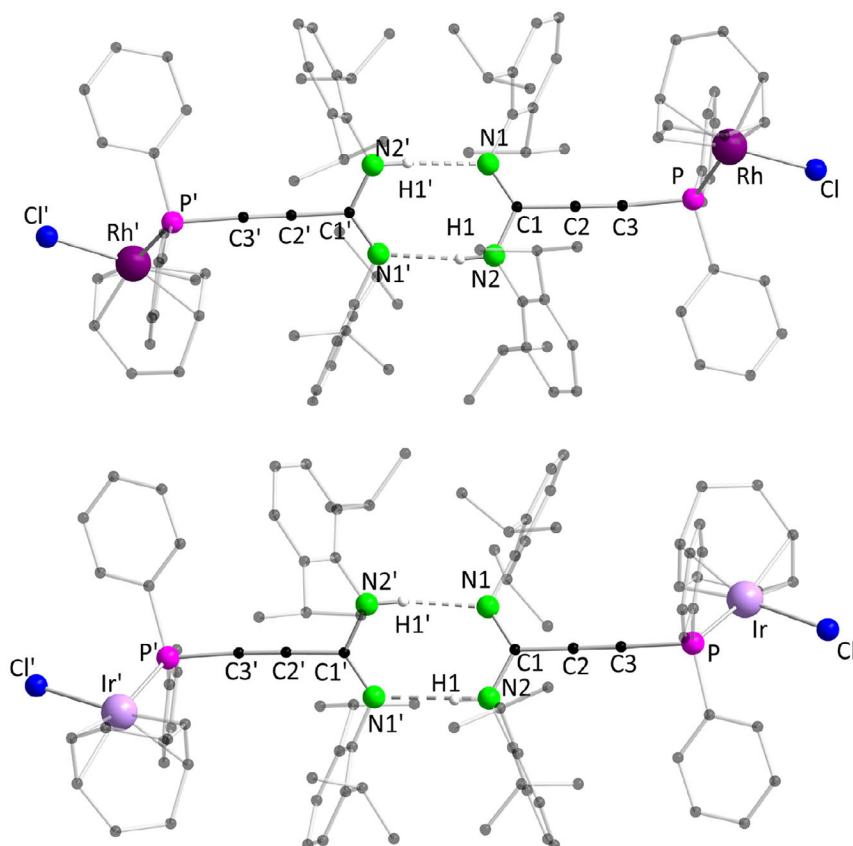
ions (Figure 4). Despite this variation, Rh–P and Ir–P bond distances were observed to be 2.285(2) Å and 2.289(13) Å, respectively, in complexes 6 and 7, which are not much different from complexes 1 and 2. The P–Rh–Cl and P–Ir–Cl bond angles were also similar to complexes 1 and 2, which were 91.2(6)° and 92.3(5)°, respectively. The complexes 6 and 7 were also seen to exist in the form of a dimer, and N–H–N units were seen interacting via hydrogen bonding with an H–N bond distance of 2.056(1) Å and 2.071(1) Å in complexes 6 and 7, respectively, which are in good agreement with the reported hydrogen bond lengths.<sup>[69]</sup>

The heteronuclear NMR analysis of complexes 6 and 7 provided further insight into their structural characteristics. The signals of 6 and 7 were observed to be broad in the  $^1\text{H}$  NMR spectra due to the hydrogen bonding and the resulting dynamics. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, a doublet at  $\delta = 12.2$  ppm and a singlet at  $\delta = 4.1$  ppm were observed for complexes 6 and 7, respectively. These chemical shift values are relatively close to those observed for complexes 1 and 2, indicating that the electronic environment around the phosphine center in these complexes remains almost similar.

Furthermore, the  $^1\text{H}$  NMR spectra of complexes 6 and 7 also displayed comparable spectral features to those of complexes 1 and 2. However, a notable difference was the presence of an additional broad peak corresponding to the NH proton of the amidinate ligand, which appeared at  $\delta = 3.31$  ppm for complex 6 and at  $\delta = 3.44$  ppm for complex 7, which was a direct consequence of the protonation of the amidinate ligand in the hydrolyzed complexes. The presence of these additional NH resonances further confirmed the successful transformation of complexes 3 and 4 into 6 and 7, respectively, through hydrolysis. Additionally, in the



**Scheme 2.** Synthesis of complexes 3–7.



**Figure 4.** Molecular structure of **6** (top) and **7** (bottom) in the solid state. Hydrogen atoms (except N–H proton) and noncoordinating solvent molecules are omitted for clarity. Thermal ellipsoid representations and structural parameters are given in the ESI (Figure S40 and S41, Supporting Information).

electrospray ionization mass spectrometry (ESI-MS) spectrum, a molecular ion peak for  $[M + H]^+$  moiety was observed at  $m/z = 819.3051$  and  $909.3598$  for complexes **6** and **7**, respectively.

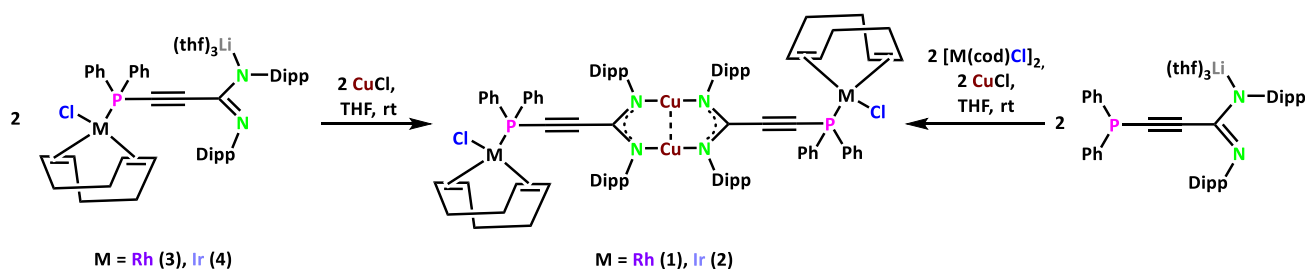
Moreover, compounds **3** and **4** were used as precursors for the synthesis of complexes **1** and **2**, which were obtained by the equimolar reaction of **3** and **4** with  $\text{CuCl}$  in THF, respectively (Scheme 3). This synthetic transformation facilitated the incorporation of copper centers into the ligand framework, giving the complexes **1** and **2** as desired products.

Finally, yet importantly, complexes **1** and **2** were also synthesized successfully via one-pot reaction using two equivalents of the lithium salt of the ligand, two equivalents of  $[\text{Rh}(\text{cod})\text{Cl}]_2$  or  $[\text{Ir}(\text{cod})\text{Cl}]_2$ , and two equivalents of  $\text{CuCl}$  in THF under ambient conditions (Scheme 3). Notably, this method proved to be highly

efficient, leading to an increase in the overall yields of complexes **1** and **2** compared to the stepwise synthetic routes. The improved yields obtained through this approach highlighted the effectiveness and practicality of the one-pot reaction for the synthesis of these metal complexes.

## 2.2. Catalytic Applications

TH catalysis is a valuable alternative to traditional hydrogenation methods, offering several key advantages.<sup>[53]</sup> It improves safety by eliminating the use of hazardous pressurized hydrogen gas, instead relying on convenient and readily available hydrogen donors such as alcohols or formic acid. Additionally, it supports



**Scheme 3.** Synthesis of complexes **1** and **2** from **3** and **4**, and a one-pot reaction.

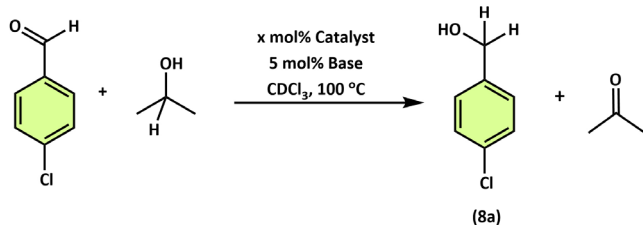


asymmetric synthesis and utilizes stable, easily accessible catalysts.<sup>[54–56]</sup> Following the successful synthesis of heterobimetallic complexes, the catalytic activity of Cu(I)–Ir(I) complex **2** was explored for the TH of aryl aldehydes, but unfortunately, Rh(I) complexes, **1** and **6** were found to be catalytically inactive. To assess the efficiency of catalyst **2**, 4-chlorobenzaldehyde was chosen as a trial substrate for the study, and isopropanol (*i*-PrOH) was used as a hydrogen transfer source. All the conversions were monitored by <sup>1</sup>H NMR spectroscopy. First of all, a blank reaction was performed using 4-chlorobenzaldehyde, *i*-PrOH, 5 mol% KOH, and without a catalyst in CDCl<sub>3</sub> at 100 °C, and no conversion to the product was observed after 120 min (Entry 1, Table 1). Under the same reaction conditions and reactants, the catalyst was added with different loading amounts from 1% to 10% (Entries 2–4, Table 1), out of which the best conversion was observed using 10 mol% of **2**. Furthermore, the same conversion was observed within 30 min as well (Entry 5, Table 1). The use of KOt-Bu was also attempted as a base instead of KOH, but the yield was as low as 22% (Entry 6, Table 1).

The catalytic performance of complex **2** was further contextualized by evaluating two other iridium based catalysts, namely [Ir(cod)ClPPh<sub>3</sub>] and complex **7**, under identical conditions. When [Ir(cod)ClPPh<sub>3</sub>] (10 mol%) was employed in the TH reaction of 4-chlorobenzaldehyde, it achieved a 71% conversion to the corresponding alcohol after 30 min (Entry 1, Table 2) while 20 mol% of [Ir(cod)ClPPh<sub>3</sub>] afforded a 97% conversion (Entry 2, Table 2). This confirmed that [Ir(cod)ClPPh<sub>3</sub>] was also an active complex for this transformation. In contrast, using 10 mol% of complex **7** resulted in 52% conversion after 30 min (Entry 3, Table 2) and 92% conversion with 20 mol% of complex **7**.

To establish that the Ir(I) center is solely responsible for the catalysis, while the sole Cu(I) center plays no active role in catalysis, a control experiment was carried out with metalloligand Cu<sub>2</sub>L<sub>2</sub> under the same conditions; virtually no conversion of 4-chlorobenzaldehyde was observed (Entry 5, Table 2). Altogether, these results underscored the comparable activity of complex **2**, with [Ir(cod)ClPPh<sub>3</sub>] and complex **7**, in terms of both conversion rate and overall reaction efficiency.

**Table 1.** Optimization of the reaction conditions by using complex **2** as a catalyst.

					
Entry <sup>a)</sup>	Catalyst [mol%]	Base (5 [mol%])	Time [min]	Conversion [%]	
1	0	KOH	120	–	
2	1	KOH	120	10	
3	5	KOH	120	37	
4	10	KOH	120	>99	
5	10	KOH	30	>99	
6	10	KOt-Bu	30	22	

<sup>a)</sup>Reaction conditions: 4-chlorobenzaldehyde (10 mg, 1 eq., 71.1 μmol), isopropanol (0.1 mL, 18.4 eq., 1.3 mmol). Base, catalyst loading and time are specified in the table above. The oil bath temperature was set at 100 °C.

**Table 2.** Screening of the catalysts [IrCl(cod)PPh<sub>3</sub>], complex **7** and metalloligand Cu<sub>2</sub>L<sub>2</sub> compared to complex **2**.

Entry <sup>a)</sup>	Catalyst	[mol%]	Time [min]	Temp [°C]	Conversion [%]
1	[IrCl(cod)PPh <sub>3</sub> ]	10	30	100	71
2	[IrCl(cod)PPh <sub>3</sub> ]	20 <sup>b)</sup>	30	100	97
3	Complex <b>7</b>	10	30	100	52
4	Complex <b>7</b>	20 <sup>b)</sup>	30	100	92
5	Cu <sub>2</sub> L <sub>2</sub>	10	30	100	–
6	Complex <b>2</b>	10	30	100	>99

<sup>a)</sup>Reaction conditions: 4-chlorobenzaldehyde (10 mg, 1 eq., 71.1 μmol), isopropanol (0.1 mL, 18.4 eq., 1.3 mmol), KOH as base (5 mol%, 3.6 μmol), catalyst loading and time are specified in the table above. The oil bath temperature was set at 100 °C. <sup>b)</sup>20 mol% of complex **7** and [IrCl(cod)PPh<sub>3</sub>] were used for the comparison of catalytic studies as they have one Ir(I) center.

After all the evaluations of optimization and screening of the catalysts, it was concluded that using 10 mol% of **2** as a catalyst at 100 °C for 30 min gives the best results for TH of 4-chlorobenzaldehyde. The substrate scope for the TH under the optimized reaction conditions was expanded to other aryl aldehydes with different electron-deficient and electron-rich substituents (Figure 5). Apparently, no particular order for the reactivity was found to be followed with the different electron-deficient and electron-rich substituents. For all the substrates, the yield was found to be more than 70%. The benzaldehyde derivatives with 4-Cl, 4-Br, 4-CF<sub>3</sub>, 2-F, and 2-Br substitutions formed the corresponding alcohols in 79%–99% yields (**8a–8f**). The catalyst also provides the selective reduction of aldehydes over potentially reducible moiety NO<sub>2</sub>, with a 94% yield of the reduced product (**8g**). A similar reaction was performed for the ketones as well (with acetophenone), but no conversion was observed even after 24 h. This observation led us to perform a reaction with a compound that has both aldehyde and ketone functionality, 3-acetylbenzaldehyde, and the product (**8k**) with reduced aldehyde was formed in 94% yield. Furthermore, benzaldehyde derivatives with electron-donating

groups like 4-Me, 4-SMe, and 2-OMe formed corresponding alcohols in 72%, 93% and 95% yield (**8h–8j**), respectively. Additionally, the catalytic activity was tested for more tough heteroaromatic compounds, 2-acetylfuran, and 2-acetylthiophene. Usually, they have the ability to coordinate to the metal center and suppress the catalytic activity,<sup>[70]</sup> however, we obtained the products (**8l–8m**) in a good yield (95%–98%).

### 2.3. Photophysical Properties

Following the applications of complex **2** in TH catalysis, the photophysical properties of the protonated amidinate ligand **5**, the heterobimetallic Cu(I)–Ir(I) complex **2**, and the Ir(I) complex **7** were investigated under identical conditions in the solid state at 77 K (Figure 6). The compound **5** exhibited a broad emission band centered at 480 nm when excited at 390 nm. Because **5** contains no metal centers, this emission is attributed to a ligand-centered excited state, likely localized on the amidine or conjugated phosphine backbone.<sup>[71]</sup> The measured phosphorescence

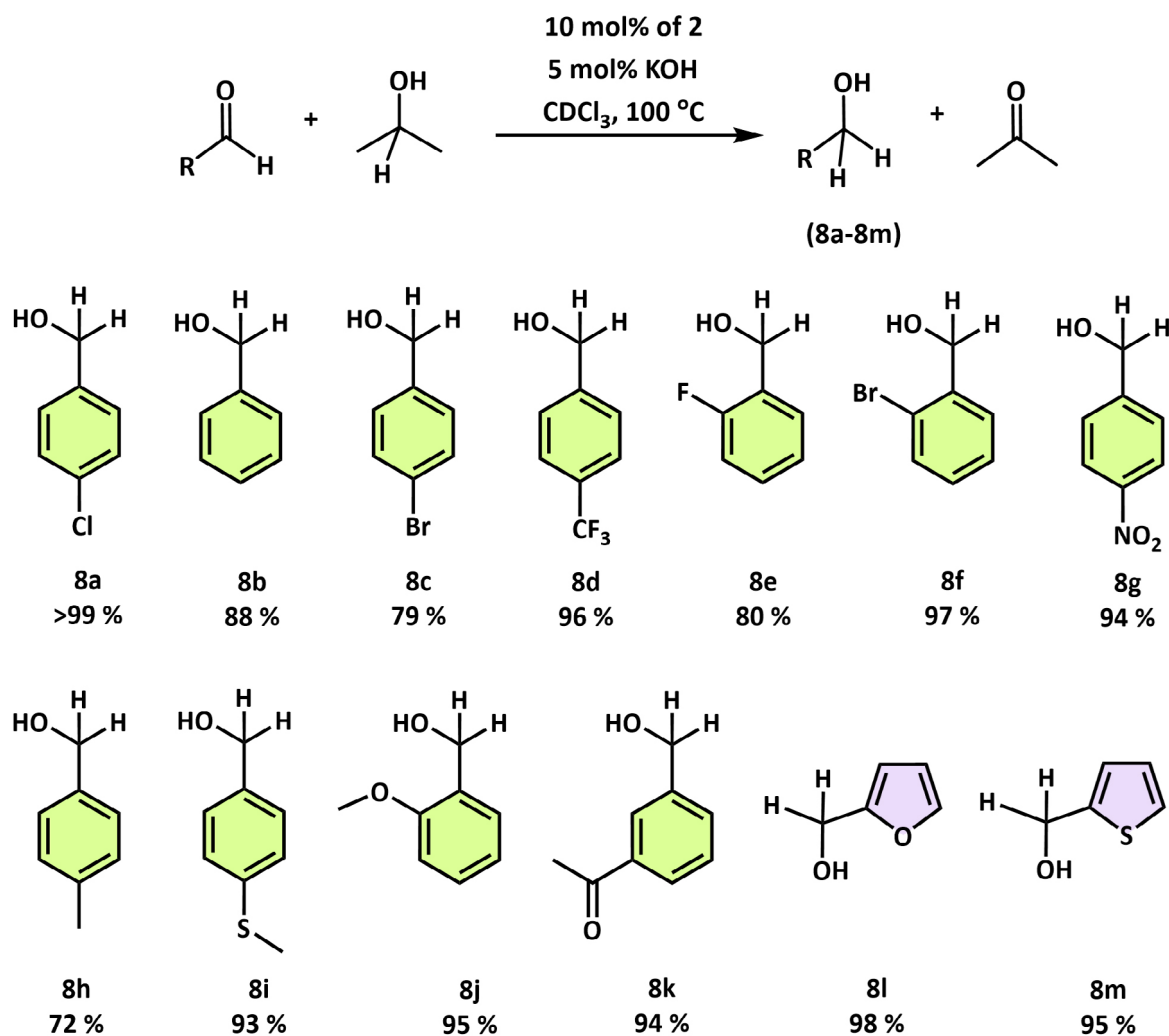
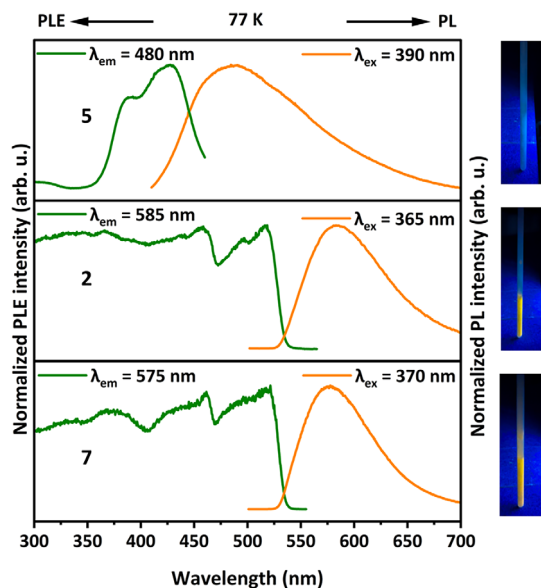


Figure 5. Screening of the substrates for TH of aldehydes catalyzed by complex **2**.



**Figure 6.** Normalized photoluminescence excitation (PLE) and emission (PL) spectra of solid samples (left) of the compounds **5**, **2**, and **7** at 77 K. Photographs of the complexes (right) under UV illumination ( $\lambda = 365$  nm) at 77 K. PLE and PL spectra were recorded at the depicted wavelengths ( $\lambda_{\text{em}}$  and  $\lambda_{\text{ex}}$ ).

lifetime of the compound **5** was observed to be below the detection limit of our detector ( $<6 \mu\text{s}$ ).

Under the same solid-state conditions, Cu(I)–Ir(I) complex **2** displays a redshifted emission compared to compound **5**, with maximum at 585 nm upon excitation at 365 nm. This shift to lower energy relative to **5** arises from a mixed metal-to-ligand charge-transfer (MLCT) transition between Ir(I) and the phosphine center, and the heavy-atom effect of Ir(I), which enhances strong spin–orbit coupling.<sup>[72,73]</sup> In this rigid environment, nonradiative relaxation is minimized, yielding a phosphorescence lifetime of compound **2** of  $7 \mu\text{s}$  (Table S2, Supporting Information). Similarly, Ir(I) complex **7** exhibits an emission maximum at 575 nm when excited at 370 nm. The emission can likewise be assigned to an Ir-centered MLCT transition. The solid-state rigidity enhances radiative decay for **7**, resulting in a longer phosphorescence lifetime of  $13 \mu\text{s}$  (Table S2, Supporting Information). In both complexes, the shape of the emission spectrum is independent of the excitation wavelength. The Cu(I)–Ir(I) complex **2** exhibits a shorter lifetime compared to complex **7**, primarily due to the excited-state flattening distortion of Cu(I) to Cu(II) upon excitation and thereby, increasing nonradiative decay rates.<sup>[74–77]</sup>

### 3. Conclusion

The study successfully demonstrated the synthesis of heterobimetallic Cu(I)–Rh(I), **1**, and Cu(I)–Ir(I), **2**, complexes through the reaction of the  $\text{Cu}_2\text{L}_2$  metalloligand with  $[\text{Rh}(\text{cod})\text{Cl}]_2$  and  $[\text{Ir}(\text{cod})\text{Cl}]_2$ , respectively, in THF. Additionally, a one-pot synthetic strategy using the lithium salt of the ligand, CuCl, and the Rh or Ir precursors led to enhanced yields of these complexes. A key structural observation

was the nonplanarity of the eight-membered  $\text{Cu}_2\text{C}_2\text{N}_4$  ring in both complexes, with torsional angles of  $19.7^\circ$  and  $19.5^\circ$ , respectively, in contrast to the completely planar  $[\{(\text{AuI})\text{Ph}_2\text{PC}\equiv\text{CC}(\text{NDipp})_2\}_2\text{Cu}_2]$  system. Further, the reaction of phosphine-substituted lithium acetylide amidinate with  $[\text{Rh}(\text{cod})\text{Cl}]_2$  and  $[\text{Ir}(\text{cod})\text{Cl}]_2$  yielded complexes **3** and **4**, which were hydrolyzed to get the corresponding protonated amidinate complexes **6** and **7**. Moreover, the lithium salt of the ligand was hydrolyzed to obtain the protonated ligand **5**, and further reaction was performed with Rh and Ir precursors to obtain the complexes **6** and **7** respectively.

The Cu(I)–Ir(I) complex **2** was explored as a catalyst for the TH of aryl aldehydes using isopropanol as a hydrogen donor source. A comparative study with other catalysts, including  $[\text{IrCl}(\text{cod})\text{PPh}_3]$  and complex **4**, showed that complex **2** exhibited superior catalytic activity, while the Rh complexes are inactive. The substrate scope of the TH reaction was further explored, revealing that benzaldehyde derivatives bearing both electron-donating and electron-withdrawing substituents were efficiently converted into their corresponding alcohols with yields exceeding 70%. Moreover, only selective reduction of the aldehydes over ketones was observed, and it also proved effective for the reduction of heteroaromatic aldehydes, such as 2-acetylfuran and 2-acetylthiophene, yielding the desired products in 95%–98%. However, no cooperative effects between the Cu and the Ir center were observed. Furthermore, complexes with Ir(I) center were found to be luminescent in the solid state at 77 K with an emission maximum around 580 nm and a lifetime of 7–13  $\mu\text{s}$ .

### Supporting Information

The authors have cited additional references within the Supporting Information.<sup>[78–80]</sup>

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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