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Synthesis of bimetallic complexes bridged by 2,6-bis(benzimidazol-2-yl) pyridine derivatives and their catalytic properties in transfer hydrogenation†

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A series of binuclear rhodium(I) and iridium(I) complexes with 2,6-bis(benzimidazol-2-yl) pyridine (bzimpy) derivatives were synthesized and characterized by elemental analysis and spectroscopic methods. The molecular and crystal structures of complex **3d** were determined by the single crystal X-ray diffraction technique. Their monometallic analogues were prepared to compare the catalytic properties of the bimetallic complexes. To determine the catalyst properties that result in a cooperative, bimetallic enhancement of the reaction rate, the systematic variation of the intermetallic distance and the ligand donor properties of the bimetallic complexes were explored based on the transfer hydrogenation reactions of ketones.

Introduction

Recently, bimetallic catalysts have been used to enhance the rate and selectivity of catalyzed reactions.[1] A bimetallic catalyst is often substantially more efficient than a monometallic catalyst with a similar structure. The increase in catalyst performance is attributed to "cooperative" interactions between the two metals and the substrate of the reaction.[2] In the literature, it has been reported that a number of bimetallic complexes contain a ligand bridging the two metal fragments. Different examples of bridged ligands have also been employed in the synthesis of bimetallic complexes.[3]

In recent years, the coordination chemistry of transition metal ions containing multidentate bis-benzimidazole derivatives has been thoroughly investigated.[4] They have drawn a great deal of attention in various areas, including medicine,[5] research on magnetic properties,[6] photochemistry,[7] materials science,[8] solution studies,[9] and homogeneous catalysis[10] owing to the versatility of their steric and electronic properties. In particular, studies on the interaction of transition metal complexes with DNA have gained prominence, because of their relevance in the development of new reagents for biotechnology and medicine.[11]

The reduction of carbonyl compounds (C=O) is an important transformation in synthetic organic chemistry since it is a general entry into alcohols.[12] While homogeneous monometallic (ruthenium, rhodium, and iridium) complexes are usually employed as catalysts,[13] far less attention has been devoted to bimetallic transition-metal-based systems.[14] Iridium complexes are preferable over those of rhodium because of their high activities and lower costs. Monometallic complexes bearing N, P, O, S, and C element-based ligands with various forms are perhaps the most classic and popular catalysts for TH.[15] The resulting complexes are neutral, mono or dicationic and form metal–donor atom bonds useful for catalytic transfer hydrogenation (TH) reactions.[15] Monometallic complexes of ruthenium with the bzimpy ligand are known to be catalytic toward TH.[16] The catalytic activities of bimetallic complexes with monometallic counterparts have been compared in TH.[17] However, to the best of our knowledge, development of a bimetallic complex of the bzimpy ligand is yet to be explored. Herein, we extend the use of the bzimpy ligand for the synthesis of bimetallic rhodium(I) and iridium(I) complexes. New bimetallic complexes were investigated in the TH of aromatic and aliphatic ketones. Their electronic and catalytic properties were compared with monometallic analogues.

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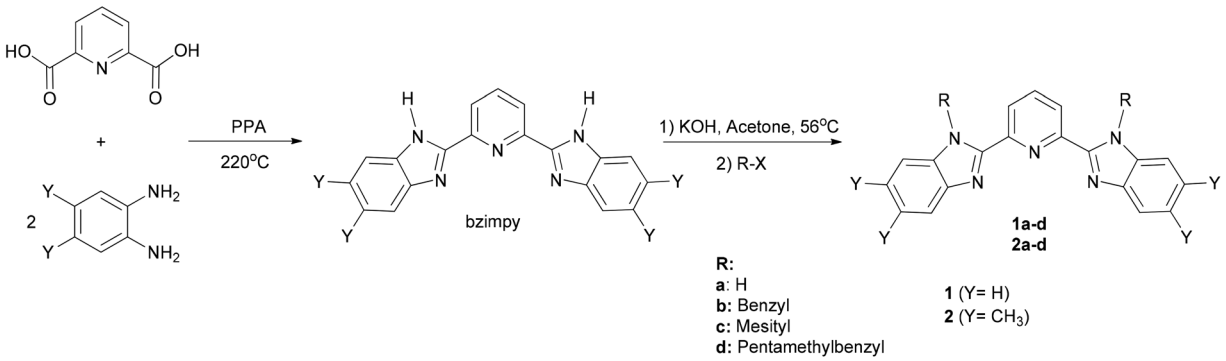
Results and discussion

Synthesis and characterization of ligands (1a–d, 2a–d)

The bzimpy ligands were synthesized according to the steps illustrated in Scheme 1. At the first step, 2,6-bis(benzimidazol-



Scheme 1 Synthesis of ligands **1a–d** and **2a–d**.

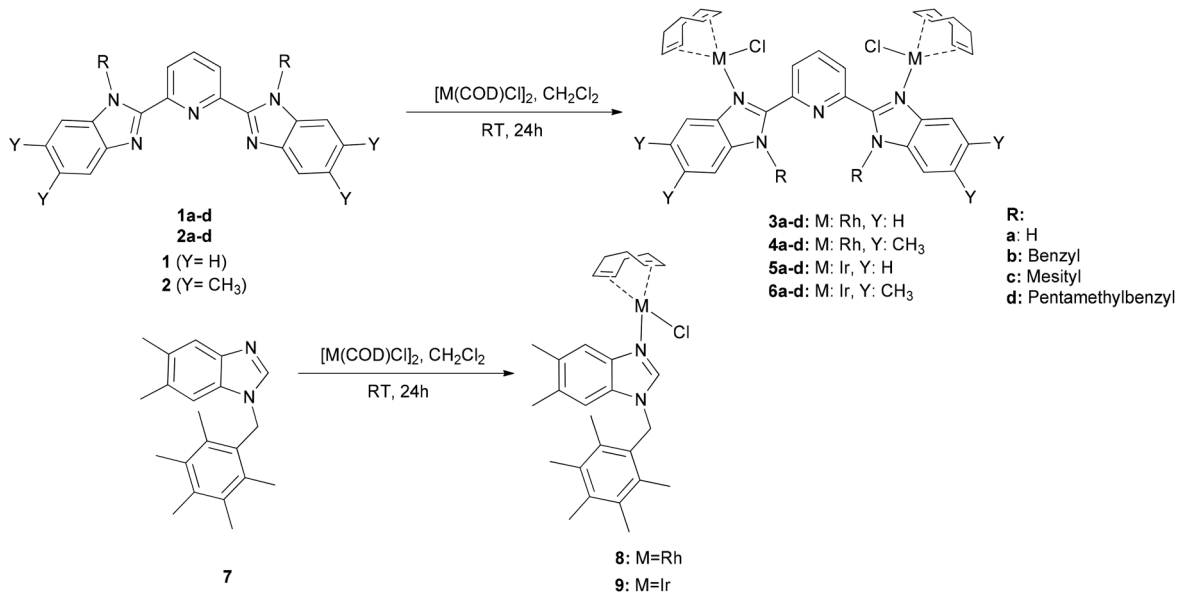
2-yl) pyridine (**1a**) and 2,6-bis(5,6-dimethylbenzimimidazol-2-yl) pyridine (**2a**) were prepared by the reaction of pyridine-2,6-dicarboxylic acid with *o*-phenylenediamine and 4,5-dimethylbenzene-1,2-diamine in polyphosphoric acid (PPA). Bzimpy ligands (**1b–d**, **2b–d**) were obtained *via* the alkylation of the compounds (**1a**, **2a**) with benzyl chloride, 2,4,6-trimethylbenzyl bromide, and pentamethyl benzyl bromide in the presence of KOH in acetone at reflux (Scheme 1). The ligands (**1b–d**, **2b–d**) were soluble in chlorinated solvents, alcohols, and DMSO. The NMR spectroscopic data of **1b–d**, **2b–d** agreed with the proposed structures.

Compounds **1a–d** and **2a–d** were characterized by one- and two-dimensional NMR spectroscopy and elemental analysis. NMR chemical shifts were found to be in good agreement with the experimental values. In the ^{1}H-NMR spectra, the Py-H_p and Py-H_m protons were observed as doublets and triplets in a 2 : 1 ratio at around δ 8.11–8.56 ppm. Signals at δ 45.8–48.1 ppm corresponded to the benzylic methylene carbon resonances for **1b–d** and **2b–d**.

Synthesis and characterization of bimetallic Rh(I)/Ir(I) complexes

We aimed at creating a general and robust methodology that could be selected for different coordination motifs with the bzimpy ligand. Bimetallic Rh(I)/Ir(I) complexes were synthesized by the reaction of $[M(COD)Cl]_2$ (M = Rh, Ir) with the ligands (**1a–d**, **2a–d**) in CH_2Cl_2 (Scheme 2). The bimetallic complexes (**3a–d**, **4a–d**, **5a–d**, **6a–d**) were characterized by one- and two-dimensional NMR spectroscopy and single-crystal X-ray diffraction (for **3d**). The NMR chemical shifts displayed good agreement with the experimental values. The ^{1}H-NMR spectra of these complexes showed some differences from their respective ligands, especially the pyridine backbone. Py-H_m and -H_p protons for **3a–d**, **4a–d**, **5a–d**, and **6a–d** complexes were observed as doublets and triplets in a 2 : 1 ratio with a general shift toward lower fields compared to their respective ligands.

Monometallic Rh(I)/Ir(I) complexes (**8**, **9**) were synthesized through the reaction of $[M(COD)Cl]_2$ with **7** in CH_2Cl_2



Scheme 2 Synthesis of bimetallic and monometallic complexes (**3a–d**, **4a–d**, **5a–d**, **6a–d**, **8**, **9**).

(Scheme 2). The complexes (**8**, **9**) were characterized by NMR spectroscopy. The NMR chemical shifts were consistent with the experimental values. The ^{1}H-NMR spectra of the NC*H*N protons of complexes (**8**, **9**) revealed singlets at δ 8.16 and 8.58 ppm respectively.

Electrochemistry

Recently, various methods have attempted to experimentally determine and compare the density of electrons on a metal atom in complexes. These methods involve studies on cyclic voltammetry and determination of CO stretching frequencies in the IR spectra of complexes. We compared the electrochemical properties of bimetallic complexes and their monometallic analogues using two different methods.

The electrochemical behaviors of the monometallic complex (**8**) and bimetallic complexes (**4a–4d**) were investigated by CV. The CV of 5.0×10^{-3} M of Rh-complexes is presented in Fig. 1.

The electrochemical responses of the complexes were very similar with both showing two-step reduction peaks and one oxidation peak. This result is in good agreement with the literature.[18] The reduction potentials of the bimetallic complexes (**4a–4d**) and monometallic complex (**8**) were determined by cyclic voltammetry (CV) in DMSO. The reduction potential of a given complex is directly related to the charge density at the metal center. When the monometallic complex (**8**) was compared to the bimetallic complexes (**4a–4d**), the reduction potential of **8** at −0.45 V for the rhodium center shifted to −0.55 V, −0.53 V, −0.54 and −0.56 V for **4a**, **4b**, **4c** and **4d** respectively. Similar results were obtained for bimetallic complexes (**4a–4d**). On the other hand, the second quasi reduction peak of the bimetallic complexes at −0.50, −0.48, −0.51 and −0.51 V may be due to the reduction of Rh(II) to Rh(I) for the (**4a–4d**) complexes, respectively. On the reverse scan, the oxidation peaks for bimetallic complexes at −0.68 V, −0.54, −0.50 and −0.45 V can be attributed to the oxidation of Rh(I) to Rh(II) for bimetallic complexes (**4a–4d**), respectively. An oxidation peak for the monometallic complex (**8**) at −0.38 V was observed. The shift of oxidation potential to a more positive value for **8** can be explained by either slower electron-transfer kinetics or chemical reaction of the complex or surface passivation of the electrode, or any combination of these effects. Comparing the first reduction potentials of **8** and **4d**, a more positive reduction peak potential was observed in complex **4d**. The reduction potential of a complex is related to the charge density on the metal. The reduction potential will shift toward more positive potential values in Rh complexes because of the smaller positive charge density on the metal.[19] Therefore, in the current study, **4d** had the smallest positive charge density on the metal and had the highest catalytic activity. This CV result was in good agreement with the catalytic experiments.

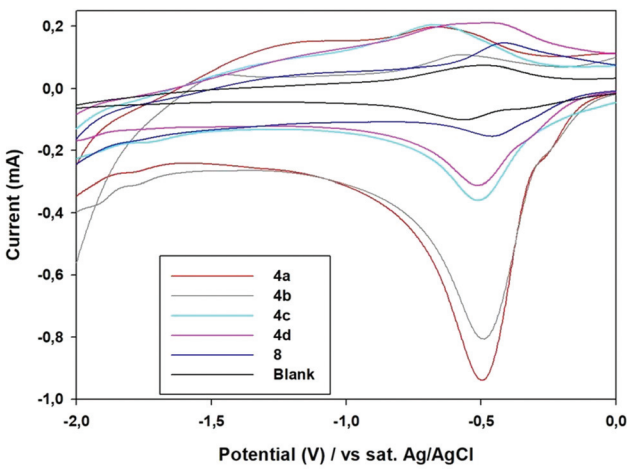


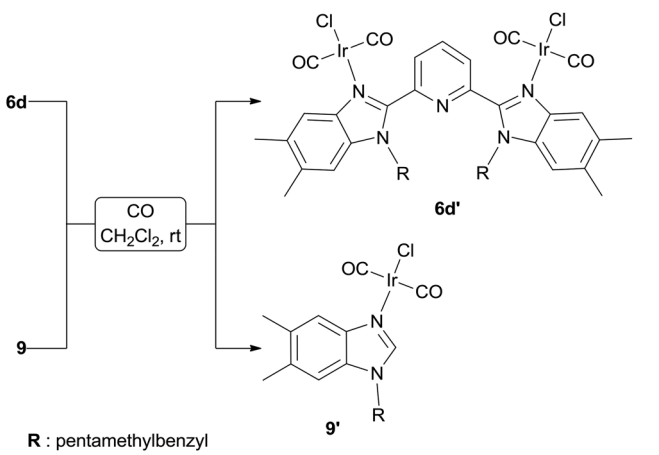
Fig. 1 Cyclic voltammogram of the blank, monometallic and bimetallic Rh(I) complexes at a platinum electrode after dissolution of 5.0×10^{-3} M of the complex in DMSO containing 0.1 M TBAB. Scan rate 100 mV s^{-1}.

Electron density comparison of 6d′ and 9′

The ν(CO) measurement of the complexes is used to determine the electron density on the metal atom in a complex. The measure of the C≡O frequency of complexes gives information about the electron donor abilities of the ligands. In this study, the monometallic (**9**) and bimetallic (**6d**) complexes were converted straightforwardly to the corresponding carbonyl derivatives **9′** and **6d′**, which allowed the electronic nature of the complexes to be inferred from IR (Scheme 3). The C–O stretching frequencies of the carbonyl complexes (**6d′**, **9′**) were recorded in CH_2Cl_2 solution. As expected, monometallic complex **9′** bearing the benzimidazole derivative exhibited CO vibrations that shifted toward a higher wave number compared to the bimetallic complex **6d′**. The complexes (**6d′**, **9′**) were characterized by IR, ^{1}H and ^{13}C-NMR. The data obtained from these methods also showed that the symmetrical ν(CO) in the respective (**6d′**, **9′**) complexes did not correlate with the catalytic activity.

Transfer hydrogenation of acetophenone catalyzed by bimetallic Rh(I)/Ir(I) complexes

TH reaction is attractive as it can avoid the use of molecular hydrogen in organic synthesis.[20] The optimum temperature

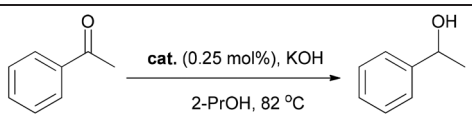


Scheme 3 Synthesis of mono- and bimetallic complexes (**6d′**, **9′**).

for catalysis is 82 °C in the presence of KOH, which is known to be the best inorganic base for this reaction.[21] Catalytic studies with bimetallic Rh(I)/Ir(I) complexes were performed for the TH of acetophenone in the presence of KOH using 2-propanol (Table 1).

Reactions were performed under identical conditions to allow the comparison of results. To investigate the time dependency of auxiliary ligands on the catalytic activity, the properties of complexes coordinated by benzyl, 2,4,6-trimethyl benzyl and pentamethyl benzyl were also studied. It was observed that the steric effect of the benzyl substituent was crucial in the bzimpy ligand type for the TH of ketones. The catalytic activity of the complexes with pentamethyl benzyl substituents (**3d**, **4d**, **5d**, and **6d**) was higher than those with a simple benzyl substituent (**3b**, **4b**, **5b**, **6b**). This result indicates that steric effects are dominant factors in this reaction, which has also been reported by other researchers.[22] The complexes (**3a**, **4a**, **5a**, **6a**) with less hindered H substitution exhibit greater reactivities compared with benzyl substituted complexes (**3b**, **3c**, **4b**, **4c**, **5b** and **5c**). Subtle differences in the coordination of the ligand may produce important differences in its electron donation, thus producing an important impact on the catalytic properties. Under the same reaction conditions, the tested methyl substituted complexes (**4**, **6**) showed greater donor strength than its non-substituted analogue in complexes (**3**, **5**). The efficiency difference between catalysts (**4**, **6**) and (**3**, **5**) could be explained by the electronic effect of benzimidazole ligands. As shown in Table 1, the bimetallic

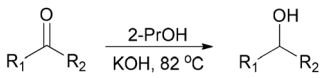
Table 1 Catalytic activity for the TH of acetophenone catalyzed by bimetallic complexes[a]



		Conversion (%)			
Entry	Cat.	10 min	15 min	30 min	60 min
1	**3a**	25	30	56	88
2	**3b**	23	25	47	82
3	**3c**	26	29	53	86
4	**3d**	29	32	58	94
5	**4a**	39	45	51	90
6	**4b**	33	36	45	84
7	**4c**	38	43	52	89
8	**4d**	54	60	82	98
9	**5a**	39	63	85	99
10	**5b**	33	44	77	94
11	**5c**	37	48	80	96
12	**5d**	41	52	90	98
13	**6a**	59	77	90	99
14	**6b**	47	61	86	96
15	**6c**	56	73	86	98
16	**6d**	78	98 (10[b])(21[c])	—	—
17	**6d**	—	84[d], 75[e], 79[f]	—	—

[a] Reaction conditions: Acetophenone (1 mmol), 2-PrOH (1 mL), KOH (0.1 mmol), catalyst (0.25 mol% based on the metal), 82 °C. [b] Room temperature. [c] 60 °C. Base. [d] NaOH. [e] K_2CO_3. [f] Cs_2CO_3.

Table 2 Catalytic activity for the TH of various ketones catalyzed by bimetallic (**4d**, **6d**) and monometallic complexes (**8**, **9**)[a]



				Conversion (%)		
Entry	R_1	R_2	Cat.	10 min	15 min	30 min
1	C_6H_5	CH_3	**4d**	54	60	82
			6d	78	98	—
			8	12	18	33
			9	22	25	38
2	C_6H_5	C_2H_5	**4d**	24	28	36
			6d	34	44	49
			8	4	6	11
			9	7	9	14
3	4-OCH_3-C_6H_4	CH_3	**4d**	42	50	67
			6d	62	89	94
			8	13	17	21
			9	17	24	32
4	3,4-diCH_3-C_6H_3	CH_3	**4d**	37	41	76
			6d	53	75	90
			8	14	19	25
			9	16	22	28
5	2-Br-C_6H_4	CH_3	**4d**	55	64	71
			6d	70	79	89
			8	21	26	37
			9	23	30	39
6	4-Br-C_6H_4	CH_3	**4d**	69	80	89
			6d	88	99	—
			8	26	32	46
			9	29	38	49
7	2-Cl-C_6H_4	CH_3	**4d**	62	68	84
			6d	81	96	—
			8	28	39	47
			9	35	43	50
8	4-Cl-C_6H_4	CH_3	**4d**	78	89	99
			6d	98	—	—
			8	28	37	48
			9	32	45	51
9	C_2H_5	CH_3	**4d**	36	43	57
			6d	49	59	72
			8	15	18	23
			9	19	24	32
10	C_3H_7	CH_3	**4d**	43	51	68
			6d	59	70	82
			8	18	21	28
			9	23	28	38
11	C_4H_9	CH_3	**4d**	48	57	76
			6d	66	79	91
			8	20	24	32
			9	26	31	43
12	CH_3	CH_3	**4d**	46	56	73
			6d	64	76	88
			8	19	22	30
			9	25	24	41
13	2-OCH_3-2-CH_3-C_3H_5	CH_3	**4d**	33	38	53
			6d	44	56	68
			8	11	17	22
			9	19	21	29
14	C_6H_{10}	—	**4d**	29	38	46
			6d	36	47	57
			8	09	16	28
			9	13	25	36
15	C_6H_5-CH_2	C_6H_5	**4d**	43	61	70
			6d	54	57	77
			8	22	30	39
			9	31	46	58

[a] Reaction conditions: Ketone (1 mmol), 2-PrOH (1 mL), KOH (0.1 mmol), catalyst (0.25 mol% based on the metal), 82 °C.

Rh(I)/Ir(I) complexes (**4d**, **6d**) were found to be the best active catalysts in the TH of acetophenone.

The effect of other bases on TH reaction was also investigated. NaOH, K_2CO_3 and Cs_2CO_3 were less efficient giving yields of 84, 75 and 79%, respectively, under the similar conditions (entry 17). After obtaining higher catalytic activities in preliminary studies, we extended our investigation to include the TH of various aromatic and aliphatic ketones. TH reactions using bimetallic complexes (**4d**, **6d**) and monometallic complexes (**8**, **9**) were performed on a series of aromatic ketones, and the results are given in Table 2. The reactions were typically carried out with 0.25 mol% of catalyst in 2-PrOH at 82 °C.

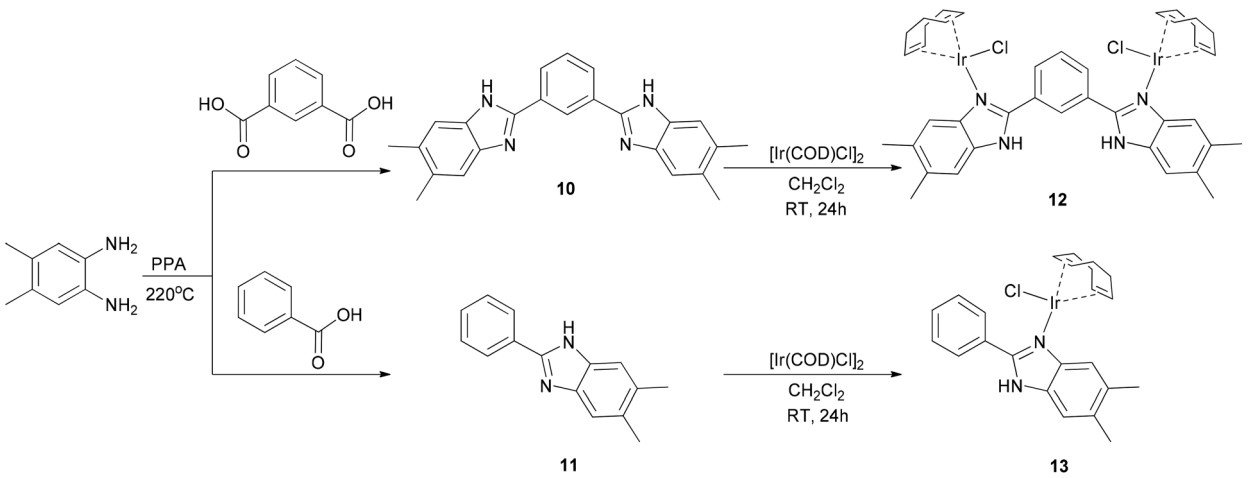
The aryl ketones were chosen to explore the effects of electronic and variations on the substrate backbone. Among the aromatic substrates examined, only the transformation of propiophenone to 1-phenylpropionol (Table 2, entry 2) required a longer reaction time for complete conversion. The position of the substituents on the phenyl ring causes significant changes in the reduction rate. On the other hand, an *ortho*- or *para*-substituted acetophenone with an electron donor substituent, such as 4-methoxy or 3,4-dimethyl, is reduced more slowly than acetophenone. For example, electron-withdrawing substituents, such as Cl and Br (entries 5–8), at the *para* position of the aryl ring of the ketone decreased the electron density of the (C═O) double bond, which improved the activity. In addition, due to steric reasons, the effect of changing the location of the substituents from the 2- to 4-position of the bromoacetophenone (entries 5 and 6) influenced the reactivity. Furthermore, this process was less efficient in the reduction of ethyl methyl ketone (entry 9) and diethyl ketone (entry 12) compared to acetophenone derivatives (entries 5–8). These differences in the catalytic activity of substituted ketones could be explained by the effects of the different steric and electronic environments.[15]

As shown in Table 2, under the same reaction conditions, it was found that the bimetallic Rh(I)/Ir(I) complexes (**4d**, **6d**) were more active catalysts than their monometallic counterparts (**8**, **9**). Chloroacetophenone resulted in a significant increase in catalytic yield (entries 7 and 8). The reduction of aliphatic ketones by monometallic and bimetallic catalysts resulted in the quantitative formation of aliphatic alcohols (entries 9–12). We also found that the alkyl length of aliphatic ketones greatly influenced the reactivity (entries 9–11). To gain insight into the effect of the basic N atom in the pyridine of the ligand and the number of benzimidazolyl subunits on the central phenyl scaffold, we synthesized 1,3-bis(benzimidazol-2-yl)benzene (m-Bimbe) **10**, 2-phenylbenzimidazole (Imbe) **11**, and their iridium complexes (**12**, **13**) (Scheme 4). The significantly decreased activity of **12** was likely the consequence of the loss of N-atom in the ligand. These results suggest that the pyridine-N atom in the ligand plays an essential role in the TH of ketones. We also investigated the number of benzimidazolyl groups on the ligand scaffold. Complex **13** (having only one benzimidazolyl) was much less active than **12** (having two benzimidazolyl subunits) (Table 3, entries 2 and 3).

Molecular structure

The crystal structure of **3d** (Fig. 2) was determined by single crystal X-ray diffraction. The title compound $\{Rh(COD)Cl\}_2L$, where L represents 2,6-bis(1-pentamethylbenzyl-1-*H*-benzimidazole-2-yl)pyridine,[23] is a bimetallic complex that consists of one and a half molecule of dichloromethane solvent in the asymmetric unit.

The complete molecular structure is generated by the implementation of the crystallographic two-fold rotation whose axis bisects the pyridine ring and crosses midway between the N3 and C4 atoms. Each benzimidazole ring connects to the [Rh(COD)Cl] units through the nitrogen atoms (N1 and N1); thus, the tridentate units act as bis-monodentate ligands in the compound. The coordination geometry around the Rh center, formed by the cyclooctadiene (COD) ligand, the N1 atom of the benzimidazole ring, and the Cl1 atom is a slightly distorted square-planar. The pyridine ring connects the Rh(I) metal centers through a N1–C1 atom bridge. The pyridine and benzimidazole rings were approximately coplanar as expected. The Rh–N and Rh–Cl bond distances were within the



Scheme 4 Synthesis of ligands (**10**, **11**) and their iridium complexes (**12**, **13**).

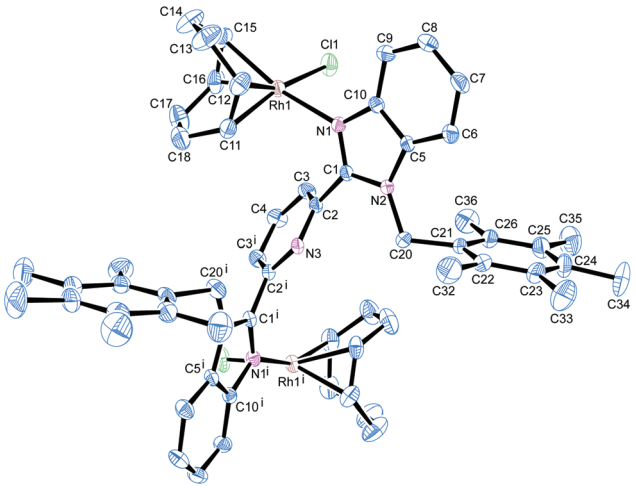
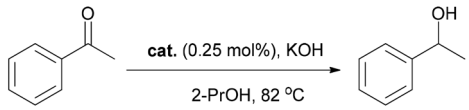


Fig. 2 The molecular structure of **3d** with displacement ellipsoids drawn at the 30% probability level and hydrogen atoms have been omitted for clarity. Symmetry code: (i) $-x, y, 1/2 - z$.

Table 3 Catalytic activity for the TH of acetophenone catalyzed by complexes **6a**, **11**, and **13**[a]



		Conversion (%)			
Entry	Cat.	10 min	15 min	30 min	60 min
1	**6a**	59	77	90	99
2	**12**	38	57	88	93
3	**13**	21	28	66	80

[a] Reaction conditions: Acetophenone (1 mmol), 2-PrOH (1 mL), KOH (0.1 mmol), catalyst (0.25 mol% based on the metal), 82 °C.

Table 4 Selected bond lengths (Å) and angles (°)[a]

Rh1···Rh1^{i}	8.083	Rh1–C11	2.101(3)
Rh1–M1	2.010	Rh1–C12	2.090(4)
Rh1–M2	1.980	Rh1–C16	2.120(4)
Rh1–N1	2.102(3)	Rh1–C15	2.127(4)
Rh1–Cl1	2.3817(10)	N3–C2	1.339(4)
N1–C1	1.320(4)	N2–C1	1.357(4)
N1–C10	1.392(4)	C2–C1	1.474(4)
N2–C5	1.393(4)	C5–C10	1.390(4)
N1–Rh1–M1	175.52	Cl1–Rh1–M2	176.61
M2–Rh1–N1	91.36	M1–Rh1–Cl1	93.49
M1–Rh1–M2	87.53	N1–Rh1–Cl1	87.88(8)
C1–N1–Rh1	126.0(2)	C10–N1–Rh1	128.0(2)

[a] M1 and M2 represent the midpoints of the olefinic bonds C15–C16 and C11–C12, respectively.

expected range and in agreement with the related complexes reported previously.[9,24] The significant bond angles and bond distances are listed in Table 4. The Rh–COD bond *trans* to benzimidazole was longer than that to chloride. This type of binding of the COD unit reveals the larger *trans* influence of the benzimidazole ligand compared to chloride. The pentamethyl benzyl ring was oriented almost perpendicular to the benzimidazole ring with a dihedral angle of 89.09(12)°. The non-coordinating central pyridine ring and the benzimidazole side arms resulted in an interplanar angle of 48.75(13)°.[25] The details of the intramolecular and intermolecular interactions are given in the ESI.†

Conclusion

We reported the preparation and characterization of a series of bimetallic Rh(I)/Ir(I) complexes (**3a–d**, **4a–d**, **5a–d**, **6a–d**) bearing monodentate ligands. Their catalytic activities were investigated for the TH reaction of ketones. The catalytic activity increased generally with the amount of electron density on the metal. Among the bimetallic complexes, catalyst **6d** demonstrated good catalytic activity, and alcohols with up to 98% conversion were obtained within 15 min. As a result, it was determined that the bimetallic complexes showed higher activity than monometallic complexes. Comparing the bimetallic complex **6d** and monometallic derivative **9** under the same reaction conditions, it is found that the former provided a good conversion (99%) while the conversion of the latter was only 25%. The CH_3 group on the benzimidazole ring had a significant effect on the catalytic activity of the complexes whereas that of benzyl, 2,4,6-trimethyl benzyl and pentamethyl benzyl at the benzimidazole ring appeared to play a less important role.

Experimental section

General consideration

Reactions involving air-sensitive components were performed using a Schlenk-type flask under an argon atmosphere with high vacuum-line techniques. The glass equipment was heated under vacuum in order to remove oxygen and moisture, and then filled with argon. The solvents were of analytical grade and distilled under an argon atmosphere from sodium (ethanol, methanol, diethyl ether, and pentane) and P_2O_5 (dichloromethane). The synthesis of bzimpy[26] and the preparation of 2,4,6-bromide and 2,3,4,5,6-pentamethylbenzyl bromide were undertaken according to the literature.[27] PPA is generally freshly prepared. Approximately 25 mL PPA was obtained by mixing 18 g P_2O_5 and 10 g 85% H_3PO_4. The reagents were stirred at 100 °C under a dry atmosphere until a homogeneous, clear viscous liquid was formed. Typically, this process takes around 24 h. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian AS400 Mercury at Ege University. As solvents, $CDCl_3$ and d_6-DMSO were employed, and the J values were in Hz.

General procedures for the synthesis of compounds 1a and 2a

Compounds **1a** and **2a** were prepared by modification of the previously published procedure.[26] Pyridine-2,6-dicarboxylic

acid (20 mmol) was stirred with *o*-phenylenediamine or 4,5-dimethylbenzene-1,2-diamine (44 mmol) in PPA (50 mL) at *ca.* 230 °C for four hours. The colored melt was poured into 500 mL of vigorously stirred cold water. The bulky blue-green precipitate was collected by filtration and treated with hot 10% aqueous Na_2CO_3 solution. It was then filtered off and dissolved in hot MeOH (~500 mL). Upon cooling, needle light-brown and pinkish crystals were filtered off and recrystallized from hot MeOH using decolorizing carbon to obtain white needle crystals.

Compound 1a: Yield: 80%. Elemental analysis: calcd (%) for $C_{19}H_{13}N_5$ (311.12): C, 73.30; H, 4.21; N, 22.49%. Found: C, 73.18; H, 4.27; N, 22.43%. ^{1}H NMR (400 MHz, 303 K DMSO-d_6) δ: 7.41 (m, 4H, BI-*H*), 7.76 (m, 4H, BI-*H*), 8.21 (t, 1H, J = 7.7 Hz, Py-H_p), 8.41 (d, 2H, J = 8.0 Hz, Py-H_m), 13.05 (2H, N–*H*). ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 7.33 (m, 4H, BI-*H*), 7.50 (m, 2H, BI-*H*), 7.88 (m, 2H, BI-*H*), 7.97 (t, 1H, J = 7.8 Hz, Py-H_p), 8.48 (d, 2H, J = 7.6 Hz, Py-H_m), 10.60 (2H, N–*H*). ^{13}C NMR (100 MHz, 303 K, DMSO-d_6) δ: 115.8, 121.6 (2 × BI-*C*), 124.3 (Py-C_m), 136.4 (Py-C_p), 140.4 (BI-*C*), 146.1 (Py-C_o), 150.5 (N=*C*-NH).

Compound 2a: Yield: 84%. Elemental analysis: calcd (%) for $C_{23}H_{21}N_5$ (367.18): C, 75.18; H, 5.76; N, 19.06%. Found: C, 74.26; H, 5.39; N, 18.74%. ^{1}H NMR (400 MHz, 303 K, DMSO-d_6) δ: 2.37 (s, 12H, BI-CH_3), 7.51 (s, 4H, BI-*H*), 8.11 (t, 1H, J = 7.7 Hz, Py-H_p), 8.26 (d, 2H, J = 8.0 Hz, Py-H_m). ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 2.28 (s, 12H, BI-CH_3), 7.21(s, 2H, BI-*H*), 7.48 (s, 2H, BI-*H*), 7.82 (t, 1H, J = 7.7 Hz, Py-H_p), 8.22 (d, 2H, J = 8.0 Hz, Py-H_m), 12.23 (2H, N–*H*). ^{13}C NMR (100 MHz, 303 K, DMSO-*d*6) δ: 22.0 (BI-*C*H$_3$), 121.6 (BI-*C*), 124.9 (Py-C_m), 130.6 (BI-*C*), 132.8 (Py-C_p), 139.5 (BI-*C*), 148.6 (Py-C_o), 151.1 (N=*C*-NH).

General procedures for the synthesis of compounds 1b–d and 2b–d

2,6-Bis(2-benzimimidazolyl)pyridine or 2,6-bis(5,6-dimethylbenzimimidazol-2-yl)pyridine (1,6 mmol) and KOH (3.36 mmol) were dissolved in acetone. The mixture was stirred and heated under reflux for one hour. Then, aryl chloride/bromide (3,2 mmol) was added and refluxed for six hours. The volatiles were removed under vacuum, and then the residue was dissolved with DCM (10 mL) and filtered with a cannula. Diethyl ether (20 mL) was added to the solution. The crystals obtained were filtered and dried under vacuum.

Compound 1b: Yield: 83%. Elemental analysis: calcd (%) for $C_{33}H_{25}N_5$ (491.21): C, 80.63; H, 5.13; N, 14.25%. Found: C, 79.91; H, 5.64; N, 13.86%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 5.55 (s, 4H, N-CH_2), 6.81 (dd, 4H, J_1 = 8.4 Hz, J_2 = 1.6 Hz, BI-*H*), 7.25 (m, 10H, Ar-*H*, 2H, BI-*H*), 7.88 (d, 2H, J = 8.0 Hz, BI-*H*), 8.01 (t, 1H, J = 7.8 Hz, Py-H_p), 8.38 (d, 2H, J = 8.0 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 48.1 (N-*C*H$_2$), 111.1, 120.5, 123.2, 124.0 (4 × BI-*C*), 125.9 (Py-C_m), 126.4, 127.6, 128.9, 136.7 (4 × Ar-*C*), 137.2 (BI-*C*), 138.5 (Py-C_p), 143.0 (BI-*C*), 149.9 (Py-C_o), 150.2 (N=*C*-NH).

Compound 1c: Yield: 85%. Elemental analysis: calcd (%) for $C_{39}H_{37}N_5$ (575.30): C, 81.36; H, 6.48; N, 12.16%. Found: C, 80.79; H, 6.56; N, 11.49%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.93 (s, 12H), 2.19 (s, 6H, Ar-CH_3), 6.26 (s, 4H, N-CH_2), 6.67 (d, 2H, J = 7.6 Hz, BI-*H*), 6.71 (s, 4H, Ar-*H*), 6.98 (t, 2H, J = 7.7 Hz, BI-*H*), 7.19 (t, 2H, J = 7.6 Hz, BI-*H*), 7.76 (d, 2H, J = 7.9 Hz, BI-*H*), 8.07 (t, 1H, J = 7.8 Hz, Py-H_p), 8.42 (d, 2H, J = 7.6 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 19.8, 19.9 (Ar-*C*H$_3$), 46.8 (N-*C*H$_2$), 105.9, 115.0, 120.6 (3 × BI-*C*), 121.1 (Py-C_m), 134.0, 135.1 (2 × Ar-*C*), 135.2 (BI-*C*), 142.0 (Py-C_p), 142.3 (BI-*C*), 149.0 (Py-C_o), 155.4 (N=*C*-NH).

Compound 1d: Yield: 82%. Elemental analysis: calcd (%) for $C_{43}H_{45}N_5$ (631.37): C, 81.74; H, 7.18; N, 11.08%. Found: C, 80.08; H, 7.06; N, 11.24%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 2.02 (s, 12H), 2.13 (s, 12H), 2.21 (s, 6H, Ar-CH_3), 6.18 (s, 4H, N-CH_2), 6.59 (d, 2H, J = 7.6 Hz), 7.01 (t, 2H, J = 7.5 Hz), 7.22 (t, 2H, J = 7.6 Hz), 7.81 (d, 2H, J = 7.6 Hz, BI-*H*), 8.11 (t, 1H, J = 7.8 Hz, Py-H_p), 8.72 (d, 2H, J = 7.8 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 15.9, 17.7, 19.9 (3 × Ar-*C*H$_3$), 47.8 (N-*C*H$_2$), 112.0, 120.0, 122.5, 123.4, 126.1 (5 × BI-*C*), 128.2, 133.4, 134.9 (3 × Ar-*C*), 136.0 (BI-*C*), 137.8 (Py-C_p), 142.4 (BI-*C*), 149.7 (Py-C_o), 150.7 (N=*C*-N).

Compound 2b: Yield: 79%. Elemental analysis: calcd (%) for $C_{37}H_{33}N_5$ (547.27): C, 81.14; H, 6.07; N, 12.79%. Found: C, 80.69; H, 6.21; N, 11.98%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 2.32 (s, 6H), 2.38 (s, 6H, BI-CH_3), 5.49 (s, 4H, N-CH_2), 6.80 (d, 4H, J = 7.3 Hz, Ar-*H*), 6.96 (s, 2H, BI-*H*), 7.19 (m, 6H, Ar-*H*), 7.62 (s, 2H, BI-*H*), 7.94 (t, 1H, J = 7.9 Hz, Py-H_p), 8.30 (d, 2H, J = 7.9 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 20.5, 20.9 (2 × BI-*C*H$_3$), 47.8 (N-*C*H$_2$), 110.9, 120.4, 125.6, 126.4 (4 × BI-*C*), 127.5 (Py-C_m), 128.9, 132.3, 133.5 (3 × Ar-*C*), 135.4 (BI-*C*), 137.7 (Ar-*C*), 138.3 (Py-C_p), 141.8 (BI-*C*), 149.7 (Py-C_o), 150.1 (N=*C*-N).

Compound 2c: Yield: 84%. Elemental analysis: calcd (%) for $C_{43}H_{45}N_5$ (631.37): C, 81.74; H, 7.18; N, 11.08%. Found: C, 81.33; H, 7.03; N, 10.97%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 2.01 (s, 12H), 2.06 (s, 6H, Ar-CH_3), 2.14 (s, 6H), 2.24 (s, 6H, BI-CH_3), 6.02 (s, 4H, N-CH_2), 6.48 (s, 2H, BI-*H*), 6.72 (s, 4H, Ar-*H*), 7.55 (s, 2H, BI-*H*), 8.01 (t, 1H, J = 7.9 Hz, Py-H_p), 8.38 (d, 2H, J = 7.9 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 20.2, 20.5 (2 × Ar-*C*H$_3$), 21.0, 21.1 (2 × BI-*C*H$_3$), 45.8 (N-*C*H$_2$), 111.9, 120.2, 125.5, 129.2 (4 × BI-*C*), 129.8 (Py-C_m), 131.7, 132.8 (2 × Ar-*C*), 134.9 (BI-*C*), 137.1 (Py-C_p), 137.6 (BI-*C*), 138.2, 141.7 (2 × Ar-*C*), 149.9 (Py-C_o), 150.5 (N=*C*-N).

Compound 2d: Yield: 86%. Elemental analysis: calcd (%) for $C_{47}H_{53}N_5$ (687.43): C, 82.05; H, 7.77; N, 10.18%. Found: C, 81.76; H, 7.51; N, 10.65%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 2.07 (s, 12H), 2.13 (s, 6H), 2.15 (s, 12H, Ar-CH_3), 2.23 (s, 6H), 2.31 (s, 6H, BI-CH_3), 6.16 (s, 4H, N-CH_2), 6.43 (s, 2H), 7.58 (s, 2H, BI-*H*), 8.04 (t, 1H, J = 7.9 Hz, Py-H_p), 8.39 (d, 2H, J = 7.9 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 16.9, 17.0, 17.3 (3 × Ar-*C*H$_3$), 20.4, 21.1 (2 × BI-*C*H$_3$), 47.4 (N-*C*H$_2$), 112.3, 120.0, 125.5, 129.3 (4 × BI-*C*), 131.6 (Py-C_m), 132.6, 133.0 (2 × Ar-*C*), 133.2 (BI-*C*), 135.2 (Py-C_p), 138.1 (BI-*C*), 141.7 (Ar-*C*), 149.9 (Py-C_o), 150.5 (N=*C*-N).

General procedures for the synthesis of complexes 3a–d, 4a–d, 5a–d, and 6a–d

$[M(COD)Cl]_2$ (0.12 mmol) in a dry dichloromethane solution (30 mL) was added under nitrogen to a dichloromethane solution (10 mL) of the ligand (0.12 mmol). The resulting solution

was stirred for 24 hours at room temperature, and the yellow precipitate was filtered off, washed with diethyl ether (20 mL), and dried in a vacuum to obtain the final product.

Complex 3a: Yield: 86%. Elemental analysis: calcd (%) for $C_{35}H_{37}Cl_2N_5Rh_2$ (803.05): C, 52.26; H, 4.64; N, 8.71%. Found: C, 51.88; H, 4.52; N, 8.58%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.33 (m, 2H), 1.45 (m, 2H), 1.76 (m, 8H), 2.24 (m, 2H, COD-CH_2), 2.58 (m, 2H, COD-CH_2, 2H, COD-CH), 3.57 (br, 2H, COD-CH), 4.81 (br, 2H, COD-CH), 4.88 (br, 2H, COD-CH), 7.02 (d, 2H, J = 7.6 Hz), 7.34 (m, 4H), 8.62 (d, 2H, J = 7.2 Hz, BI-H), 8.87 (t, 1H, J_1 = 7.6 Hz, J_2 = 8.0 Hz, Py-H_p), 10.71 (d, 2H, J = 8.0 Hz, Py-H_m).

Complex 3b: Yield: 84%. Elemental analysis: calcd (%) for $C_{49}H_{49}Cl_2N_5Rh_2$ (983.15): C, 59.77; H, 5.02; N, 7.11%. Found: C, 59.12; H, 5.36; N, 6.88%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.37 (m, 2H), 1.49 (m, 2H), 1.77 (m, 8H), 2.26 (m, 2H, COD-CH_2), 2.58 (m, 2H, COD-CH_2, 2H, COD-CH), 3.57 (br, 2H), 4.81 (br, 2H), 4.88 (br, 2H, COD-CH), 4.97 (d, 2H, J = 16.4), 5.37 (d, 2H, J = 15.6, N-CH_2), 6.67 (d, 2H, J = 8.0 Hz, Ar-H), 7.02 (t, 4H, J_1 = 7.2 Hz, J_2 = 7.6 Hz), 7.13 (t, 4H, J_1 = 7.2 Hz, J_2 = 6.8 Hz, Ar-H), 7.34 (d, 2H, J = 8.2 Hz), 7.44 (t, 2H, J_1 = 7.2 Hz, J_2 = 6.8 Hz), 7.55 (t, 2H, J_1 = 7.2 Hz, J_2 = 6.8 Hz, BI-H), 8.63 (t, 1H, J_1 = 7.6 Hz, J_2 = 8.0 Hz, Py-H_p), 8.77 (d, 2H, J = 8.0 Hz, BI-H), 10.16 (d, 2H, J = 8.0 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 29.8, 30.1, 30.7, 31.9 (4 × COD-CH$_2$), 48.2 (N-CH$_2$), 75.3 (d, J = 13.2 Hz), 76.3 (d, J = 14.1 Hz), 83.8 (d, J = 10.7 Hz), 84.6 (d, J = 11.3 Hz, COD-CH), 110.8, 120.9, 124.5, 125.4 (4 × BI-C), 125.9 (Py-C_m), 127.7 (Ar-C), 128.9 (Py-C_m), 135.2 (Ar-C), 136.0 (BI-C), 137.9 (Py-C_p), 140.6 (Ar-C), 142.2 (BI-C), 147.6 (Py-C_o), 148.4 (N=C-N).

Complex 3c: Yield: 87%. Elemental analysis: calcd (%) for $C_{55}H_{61}Cl_2N_5Rh_2$ (1067.24): C, 61.81; H, 5.75; N, 6.55%. Found: C, 62.29; H, 5.89; N, 6.40%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.40–2.62 (m, 18H, Ar-CH_3, 2H, COD-CH, 16H, COD-CH_2), 3.56 (br, 2H), 4.77 (br, 2H), 4.89 (br, 2H, COD-CH), 5.53 (d, 2H, J = 14.8), 5.74 (d, 2H, J = 15.2, N-CH_2), 6.72 (d, 2H, J = 8.8 Hz, BI-H), 6.78 (s, 4H, Ar-H), 7.14 (t, 2H, J_1 = 7.8 Hz, J_2 = 8.0 Hz), 7.38 (t, 2H, J_1 = 7.6 Hz, J_2 = 7.6 Hz), 8.64 (d, 2H, J = 7.6 Hz, BI-H), 8.79 (t, 1H, J_1 = 7.8 Hz, J_2 = 8.0 Hz, Py-H_p), 10.23 (d, 2H, J = 8.0 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 20.2, 20.9 (2 × Ar-CH$_3$), 29.7, 30.1, 30.8, 31.8 (4 × COD-CH$_2$), 45.9 (N-CH$_2$), 74.8, 76.0, 84.6, 84.8 (br, 4 × COD-CH), 112.0, 120.6, 124.1, 124.9 (4 × BI-C), 127.5 (Ar-C), 129.9 (Py-C_m), 134.3, 137.0 (2 × Ar-C), 137.9 (Py-C_p), 138.4, 140.8 (2 × BI-C), 148.6 (Py-C_o), 149.1 (N=C-N).

Complex 3d: Yield: 89%. Elemental analysis: calcd (%) for $C_{59}H_{69}Cl_2N_5Rh_2$ (1123.30): C, 62.99; H, 6.18; N, 6.23%. Found: C, 62.76; H, 6.02; H, 5.91%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.37–2.65 (m, 30H, Ar-CH_3, 2H, COD-CH, 16H, COD-CH_2), 3.55 (br, 2H), 4.77 (br, 2H), 4.90 (br, 2H, COD-CH), 5.52 (d, 2H, J = 15.2), 5.96 (d, 2H, J = 15.2, N-CH_2), 6.51 (d, 2H, J = 8.8 Hz), 7.06 (t, 2H, J_1 = 7.2 Hz, J_2 = 8.0 Hz), 7.36 (t, 2H, J_1 = 7.6 Hz, J_2 = 7.6 Hz), 8.59 (d, 2H, J = 8.4 Hz, BI-H), 8.85 (t, 1H, J_1 = 7.6 Hz, J_2 = 8.0 Hz, Py-H_p), 10.22 (d, 2H, J = 8.0 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 16.9, 17.3, 19.9 (3 × Ar-CH$_3$), 29.9, 30.1, 30.7, 31.8 (4 × COD-CH$_2$), 47.4 (N-CH$_2$), 74.7 (d, J = 12.8 Hz), 75.9 (d, J = 13.6 Hz), 84.6 (d, J = 11.3 Hz), 84.9 (d, J = 11.7 Hz, COD-CH), 112.5, 120.4, 123.9, 124.8 (4 × BI-C), 127.6 (Ar-C), 130.0 (Py-C_m), 133.1, 133.4 (2 × Ar-C), 136.2 (BI-C), 138.0 (Py-C_p), 140.9 (BI-C), 148.4 (Py-C_o), 148.8 (N=C-N).

Complex 4a: Yield: 79%. Elemental analysis: calcd (%) for $C_{39}H_{45}Cl_2N_5Rh_2$ (859.12): C, 54.43; H, 5.27; N, 8.14%. Found: C, 54.11; H, 5.12; N, 8.03%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.32 (m, 2H), 1.41 (m, 2H), 1.79 (m, 8H, COD-CH_2), 2.18–2.68 (m, 12H, BI-CH_3, 6H, COD-CH_2), 3.58 (br, 2H), 4.79 (br, 2H), 4.86 (br, 2H, COD-CH), 7.04 (s, 2H), 8.51 (s, 2H, BI-H), 8.76 (t, 1H, J_1 = 7.6 Hz, J_2 = 8.0 Hz, Py-H_p), 10.58 (d, 2H, J = 7.9 Hz, Py-H_m).

Complex 4b: Yield: 81%. Elemental analysis: calcd (%) for $C_{53}H_{57}Cl_2N_5Rh_2$ (1039.21): C, 61.16; H, 5.52; N, 6.73%. Found: C, 60.05; H, 5.62; N, 6.78%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.31 (m, 2H), 1.43 (m, 2H), 1.77 (m, 8H, COD-CH_2), 2.18–2.68 (m, 12H, BI-CH_3, 4H, COD-CH_2, 2H, COD-CH), 3.57 (br, 2H), 4.75 (br, 2H), 4.86 (br, 2H, COD-CH), 4.93 (d, 2H, J = 16.4), 5.32 (d, 2H, J = 16.4, N-CH_2), 6.65 (d, 4H, J = 6.8 Hz),7.02 (t, 4H, J_1 = 7.2 Hz, J_2 = 6.8 Hz, Ar-H), 7.07 (s, 2H, BI-H), 7.12 (t, 4H, J_1 = 7.6 Hz, J_2 = 7.2 Hz, Ar-H), 8.46 (s, 2H, BI-H), 8.56 (t, 1H, J_1 = 7.6 Hz, J_2 = 8.0 Hz, Py-H_p), 10.09 (d, 2H, J = 8.0 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 20.6, 20.8 (2 × BI-CH$_3$), 29.9, 30.4, 30.8, 31.9 (4 × COD-CH$_2$), 47.9 (N-CH$_2$), 75.2 (d, J = 13.1 Hz), 76.1 (d, J = 13.7 Hz), 84.4 (d, J = 10.7 Hz), 84.7 (d, J = 11.4 Hz, COD-CH), 110.5, 120.4, 125.8, 127.5 (4 × BI-C), 128.6 (Py-C_m), 128.8, 133.8, 133.9 (3 × Ar-C), 135.2 (BI-C), 136.3 (Ar-C), 137.6 (Py-C_p), 139.2 (BI-C), 147.4 (Py-C_o), 147.7 (N=C-N).

Complex 4c: Yield: 85%. Elemental analysis: calcd (%) for $C_{59}H_{69}Cl_2N_5Rh_2$ (1123.30): C, 62.99; H, 6.18; N, 6.23%. Found: C, 61.43; H, 6.01; N, 6.08%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.35–2.55 (m, 18H, Ar-CH_3, 12H,BI-CH_3, 2H, COD-CH, 16H, COD-CH_2), 3.56 (br, 2H), 4.73 (br, 2H), 4.88 (br, 2H, COD-CH), 5.52 (d, 2H, J = 14.8), 5.64 (d, 2H, J = 15.2, N-CH_2), 6.50 (s, 2H, BI-H), 6.75 (s, 4H, Ar-H), 8.34 (s, 2H, BI-H), 8.71 (t, 1H, J_1 = 7.2 Hz, J_2 = 8.0 Hz, Py-H_p), 10.17 (d, 2H, J = 8.0 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 20.1, 20.5 (2 × Ar-CH$_3$), 20.8, 20.9 (2 × BI-CH$_3$), 29.8, 30.6, 30.9, 31.9 (4 × COD-CH$_2$), 45.6 (N-CH$_2$), 74.7 (d, J = 13.1 Hz), 75.9 (d, J = 13.7 Hz), 84.3 (d, J = 10.7 Hz), 84.5 (d, J = 11.4 Hz, COD-CH), 111.8, 120.0, 127.8 (3 × BI-C), 129.3 (Py-C_m), 129.8 (BI-C), 133.0, 133.4 (2 × Ar-C), 134.4, 137.0 (2 × BI-C), 137.6 (Py-C_p), 138.1 (Ar-C), 139.4 (Ar-C), 148.2 (Py-C_o), 148.6 (N=C-N).

Complex 4d: Yield: 86%. Elemental analysis: calcd (%) for $C_{63}H_{77}Cl_2N_5Rh_2$ (1179.37): C, 64.07; H, 6.57; N, 5.93%. Found: C, 63.71; H, 6.38; N, 6.01%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.38–2.61 (m, 30H, Ar-CH_3, 12H, BI-CH_3, 2H, COD-CH, 16H, COD-CH_2), 3.54 (br, 2H), 4.72 (br, 2H), 4.89 (br, 2H), 5.49 (d, 2H, J = 15.2), 5.88 (d, 2H, J = 15.2), 6.27 (s, 2 H), 8.28 (s, 2 H, BI-H), 8.79 (t, 1H, J_1 = 7.2 Hz, J_2 = 8.0 Hz, Py-H_p), 10.16 (d, 2H, J = 8.0 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 16.8, 16.9, 17.2 (3 × Ar-CH$_3$), 20.4, 20.5 (2 × BI-CH$_3$), 29.8, 30.6, 30.8, 31.9 (4 × COD-CH$_2$), 47.1 (N-CH$_2$), 74.7 (d, J = 13.8 Hz), 75.9 (d, J = 13.8 Hz), 84.3 (d, J = 11.4 Hz), 84.7 (d, J = 11.4 Hz, COD-CH), 112.4, 119.7, 127.9 (3 × BI-C), 129.7 (Py-C_m), 133.0 (BI-C), 133.2, 133.3 (2 × Ar-C), 134.1, 136.0 (2 × BI-C), 137.8 (Py-C_p), 139.6 (Ar-C), 148.1 (Py-C_o), 148.9 (N=C-N).

Complex 5a: Yield: 86%. Elemental analysis: calcd (%) for $C_{35}H_{37}Cl_2N_5Ir_2$ (983.04): C, 42.76; H, 3.79; N 7.12%. Found: C, 42.88; H, 4.01; N, 7.18%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.72 (m, 2H), 1.78 (m, 2H), 1.81 (m, 8H), 2.30 (m, 2H, COD-CH_2), 2.55 (m, 2H, COD-CH_2, 2H, COD-CH), 3.61 (br, 2H), 4.66 (br, 2H), 4.74 (br, 2H, COD-CH), 7.43 (m, 6H), 7.87 (m, 2H, BI-H), 8.57 (t, 1H, J_1 = 7.6 Hz, J_2 = 8.0 Hz, Py-H_p), 10.95 (d, 2H, J = 8.0 Hz, Py-H_m).

Complex 5b: Yield: 84%. Elemental analysis: calcd (%) for $C_{49}H_{49}Cl_2N_5Ir_2$ (1163.29): C, 50.59; H, 4.25; N, 6.02%. Found: C, 49.68; H, 4.38; N, 6.19%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.42 (m, 2H), 1.48 (m, 2H), 1.73 (m, 8H), 2.29 (m, 2H, COD-CH_2), 2.58 (m, 2H, COD-CH_2, 2H, COD-CH), 3.21 (br, 2H), 4.42 (br, 2H), 4.62 (br, 2H), 5.48 (d, 2H, J = 15.2), 5.70 (d, 2H, J = 15.2, N-CH_2), 6.55 (d, 2H, J = 8.0 Hz), 7.07 (t, 2H, J_1 = 7.2 Hz, J_2 = 7.6 Hz, BI-H), 7.13 (m, 6H, Ar-H), 7.34 (t, 2H, J_1 = 7.2 Hz, J_2 = 7.6 Hz, BI-H), 7.44 (d, 2H, J = 7.2 Hz), 7.55 (d, 2H, J = 7.2 Hz, Ar-H), 8.38 (d, 2H, J = 8.0 Hz, BI-H), 8.53 (t, 1H, J_1 = 7.6 Hz, J_2 = 8.0 Hz, Py-H_p), 9.76 (d, 2H, J = 8.0 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 29.6, 30.4, 31.9, 32.3 (4 × COD-CH_2), 47.2 (N-CH_2), 56.3 (d, J = 13.2 Hz), 58.1 (d, J = 14.1 Hz), 69.2 (d, J = 10.7 Hz), 70.3 (d, J = 11.3 Hz, COD-CH), 102.3, 119.8, 126.7 (3 × BI-C), 129.6 (Py-C_m), 132.7 (BI-C), 133.2, 134.9 (2 × Ar-C), 138.1, 139.7 (2 × BI-C), 140.9 (Py-C_p), 141.8 (Ar-C), 149.8 (Py-C_o), 149.9 (N=C-N).

Complex 5c: Yield: 87%. Elemental analysis: calcd (%) for $C_{55}H_{61}Cl_2N_5Ir_2$ (1247.45): C, 52.96; H, 4.93; N, 5.61%. Found: C, 53.18; H, 5.19; N 5.88%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.42–2.66 (m, 18H, Ar-CH_3, 2H, COD-CH, 16H, COD-CH_2), 3.52 (br, 2H), 4.44 (br, 2H), 4.68 (br, 2H), 5.50 (d, 2H, J = 14.8), 5.69 (d, 2H, J = 15.2, N-CH_2), 6.72 (d, 2H, J = 8.8 Hz, BI-H), 6.78 (s, 4H, Ar-H), 7.14 (t, 2H, J_1 = 7.8 Hz, J_2 = 8.0 Hz), 7.38 (t, 2H, J_1 = 7.6 Hz, J_2 = 7.6 Hz), 8.44 (d, 2H, J = 7.6 Hz, BI-H), 8.79 (t, 1H, J_1 = 7.8 Hz, J_2 = 8.0 Hz, Py-H_p), 10.23 (d, 2H, J = 8.0 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 21.3, 21.5 (2 × Ar-CH_3), 31.8, 32.5, 32.6, 34.0 (4 × COD-CH_2), 46.9 (N-CH_2), 58.3, 59.7, 69.7, 70.9 (4 × COD-CH), 113.0, 121.0, 128.7 (3 × BI-C), 130.9 (Py-C_m), 131.0 (BI-C), 133.8, 134.7 (2 × Ar-C), 135.8, 136.3 (2 × BI-C), 138.2 (Py-C_p), 139.5 (Ar-C), 140.2 (Py-C_o), 148.9 (N=C-N).

Complex 5d: Yield: 89%. Elemental analysis: calcd (%) for $C_{59}H_{69}Cl_2N_5Ir_2$ (1303.55): C, 54.36; H, 5.34; N, 5.37%. Found: C, 54.71; H, 5.48; N 5.57%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.37–2.65 (m, 30H, Ar-CH_3, 2H, COD-CH, 16H, COD-CH_2), 3.55 (br, 2H), 4.77 (br, 2H), 4.90 (br, 2H, COD-CH), 5.52 (d, 2H, J = 15.2), 5.96 (d, 2H, J = 15.2, N-CH_2), 6.55 (d, 2H, J = 8.8 Hz), 7.06 (t, 2H, J_1 = 7.2 Hz, J_2 = 8.0 Hz), 7.32 (t, 2H, J_1 = 7.6 Hz, J_2 = 7.6 Hz), 8.38 (d, 2H, J = 8.4 Hz, BI-H), 8.52 (t, 1H, J_1 = 7.6 Hz, J_2 = 8.0 Hz, Py-H_p), 9.76 (d, 2H, J = 8.0 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 16.9, 17.1, 17.2 (3 × Ar-CH_3), 30.8, 31.2, 31.6, 32.6 (4 × COD-CH_2), 47.4 (N-CH_2), 57.3, 58.6, 69.1, 69.8 (4 × COD-CH), 112.5, 120.2 (2 × BI-C), 123.9, 125.0 (2 × Ar-C), 127.5 (BI-C), 130.6 (Py-C_m), 133.1 (BI-C), 133.2, 133.5 (2 × Ar-C), 134.1, 136.3 (2 × BI-C), 136.6 (Py-C_p), 140.5 (Ar-C), 148.1 (Py-C_o), 148.5 (N=C-N).

Complex 6a: Yield: 79%. Elemental analysis: calcd (%) for $C_{39}H_{45}Cl_2N_5Ir_2$ (1039.15): C, 45.08; H, 4.36; N, 6.75%. Found: C, 45.11; H, 4.42; N, 6.83%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.32 (m, 2H), 1.41 (m, 2H), 1.79 (m, 8H, COD-CH_2), 2.18–2.68 (m, 12H, BI-CH_3, 4H, COD-CH_2, 2H, COD-CH), 3.41 (br, 2H), 4.62 (br, 2H), 4.83 (br, 2H, COD-CH), 6.72 (s, 2H), 8.32 (s, 2H, BI-H), 8.61 (t, 1H, J_1 = 7.6 Hz, J_2 = 8.0 Hz, Py-H_p), 9.91 (d, 2H, J = 7.9 Hz, Py-H_m).

Complex 6b: Yield: 81%. Elemental analysis: calcd (%) for $C_{53}H_{57}Cl_2N_5Ir_2$ (1219.39): C, 52.20; H, 4.71; N, 5.74%. Found: C, 52.38; H, 4.92; N, 5.78%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.34 (m, 2H), 1.46 (m, 2H), 1.79 (m, 8H, COD-CH_2), 2.23–2.76 (m, 12H, BI-CH_3, 4H, COD-CH_2, 2H, COD-CH), 3.37 (br, 2H), 4.45 (br, 2H), 4.66 (br, 2H, COD-CH), 4.94 (d, 2H, J = 16.4), 5.32 (d, 2H, J = 16.4, N-CH_2), 6.63 (d, 2H, J = 6.8 Hz), 7.04 (t, 4H, J_1 = 7.2 Hz, J_2 = 6.8 Hz, Ar-H), 7.09 (s, 2H, BI-H), 7.14 (t, 4H, J_1 = 7.6 Hz, J_2 = 7.2 Hz, Ar-H), 8.37 (s, 2H, BI-H), 8.46 (t, 1H, J_1 = 7.6 Hz, J_2 = 8.0 Hz, Py-H_p), 9.79 (d, 2H, J = 8.0 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 23.1, 23.4 (2 × BI-CH_3), 33.7, 34.3, 34.4, 35.8 (4 × COD-CH_2), 48.7 (N-CH_2), 60.2, 61.6, 71.6, 72.7 (4 × COD-CH), 114.9, 122.8, 130.6 (3 × BI-C), 135.7 (Py-C_m), 136.6, 137.7, 133.9 (3 × Ar-C), 139.4, 140.1 (2 × BI-C), 141.3 (Py-C_p), 142.1 (Ar-C), 150.8 (Py-C_o), 150.9 (N=C-N).

Complex 6c: Yield: 85%. Elemental analysis: calcd (%) for $C_{59}H_{69}Cl_2N_5Ir_2$ (1303.55): C, 54.36; H, 5.34; N, 5.37%. Found: C, 54.43; H, 5.42; N, 5.48%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.26–2.38 (m, 18H, Ar-CH_3, 12H, BI-CH_3, 2H, COD-CH, 16H, COD-CH_2), 3.21 (br, 2H), 4.42 (br, 2H), 4.62 (br, 2H, COD-CH), 5.49 (d, 2H, J = 14.8), 5.70 (d, 2H, J = 15.2, N-CH_2), 6.52 (s, 2H, BI-H), 6.80 (s, 4H, Ar-H), 8.19 (s, 2H, BI-H), 8.43 (t, 1H, J_1 = 7.2 Hz, J_2 = 8.0 Hz, Py-H_p), 9.71 (d, 2H, J = 8.0 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 20.1, 20.4 (2 × Ar-CH_3), 20.8, 20.9 (2 × BI-CH_3), 30.7, 31.3, 31.5, 32.8 (4 × COD-CH_2), 45.7 (N-CH_2), 57.2, 58.6, 68.6, 69.7 (4 × COD-CH), 111.9, 119.9, 127.6 (3 × BI-C), 129.8 (Py-C_m), 130.0 (BI-C), 132.7, 133.6 (2 × Ar-C), 134.7, 137.1 (2 × BI-C), 138.3 (Py-C_p), 139.1 (Ar-C), 147.8 (Py-C_o), 147.9 (N=C-N).

Complex 6d: Yield: 86%. Elemental analysis: calcd (%) for $C_{63}H_{77}Cl_2N_5Ir_2$ (1359.48): C, 55.65; H, 5.71; N, 5.15%. Found: C, 54.21; H, 5.52; N, 5.03%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.19–1.49 (m, 8H, COD-CH_2), 1.91–2.35 (m, 30H, Ar-CH_3, 12H, BI-CH_3, 2H, COD-CH, 8H, COD-CH_2), 3.18 (br, 2H), 4.40 (br, 2H), 4.64 (br, 2H, COD-CH), 5.49 (d, 2H, J = 15.2), 5.91 (d, 2H, J = 15.2, N-CH_2), 6.29 (s, 2H), 8.07 (s, 2H, BI-H), 8.46 (t, 1H, J_1 = 7.6 Hz, J_2 = 8.0 Hz, Py-H_p), 9.72 (d, 2H, J = 8.0 Hz, Py-H_m). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 16.8, 16.9, 17.2 (3 × Ar-CH_3), 20.3, 20.8 (2 × BI-CH_3), 30.7, 31.4, 32.8 (4 × COD-CH_2), 47.2 (N-CH_2), 57.2, 58.6, 68.5, 69.8 (4 × COD-CH), 112.4, 119.6, 127.8 (3 × BI-C), 130.2 (Py-C_m), 133.0 (BI-C), 133.2, 133.3 (2 × Ar-C), 134.1, 136.0 (2 × BI-C), 136.7 (Py-C_p), 139.1 (Ar-C), 148.1 (Py-C_o), 148.9 (N=C-N).

Synthesis of compound 7

This ligand was prepared in the same manner as **2d** using 5,6-dimethyl-1H-benzimidazole (0.146 g; 1 mmol) and pentamethylbenzyl bromide (0.241 g; 1 mmol). White crystals were obtained. Yield: 86%. Elemental analysis: calcd (%) for $C_{21}H_{26}N_2$ (306.44): C, 82.31; H, 8.55, N, 9.14%. Found: C,

82.18; H, 8.49; N, 9.07%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.21 (s, 6H), 2.26 (s, 6H), 2.32 (s, 3H, Ar-CH_3), 2.45 (s, 3H), 2.47 (s, 3H, BI-CH_3), 5.26 (s, 4H, N-CH_2), 7.29 (s, 1H), 7.33 (s, 1H, BI-*H*), 7.60 (s, 1H, N=C*H*-N). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.5, 16.8, 17.1, 20.3, 20.6 (5 × BI-CH_3), 44.2 (N-CH_2), 109.7, 120.3, 127.4, 131.1, 131.2 (5 × BI-*C*), 132.8, 133.3, 133.5, 136.0 (4 × Ar-*C*), 141.1 (BI-*C*), 142.8 (N=*C*H-N).

General procedures for the synthesis of complexes 8 and 9

$[M(COD)Cl]_2$ (0.12 mmol) in a dry dichloromethane solution (30 mL) was added under nitrogen to a dichloromethane solution (10 mL) of the ligand (0.24 mmol). The resulting solution was stirred for 24 hours at room temperature, and then, the yellow precipitate was filtered off, washed with diethyl ether (20 mL), and dried in a vacuum to obtain the final product.

Complex 8: Yield: 81%. Elemental analysis: calcd (%) for $C_{29}H_{38}ClN_2Rh$ (552.98): C, 62.99; H, 6.93; N, 5.07%. Found: C, 62.81; H, 6.82; N, 4.99%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.76 (m, 4H, COD-CH_2), 2.14 (s, 6H), 2.28 (s, 6H), 2.33 (s, 3H, Ar-CH_3), 2.42 (s, 3H, BI-CH_3), 2.47 (br, 3H, BI-CH_3, 4H, COD-CH_2), 3.53 (br, 2H), 4.66 (br, 2H, COD-C*H*), 5.20 (s, 2H, N-CH_2), 7.27 (s, 1H), 7.32 (s, 1H, BI-*H*), 8.16 (s, 1H, N=C*H*-N). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.5, 16.9, 17.2 (3 × Ar-CH_3), 20.4, 20.6 (2 × BI-CH_3), 30.5, 31.5 (2 × COD-CH_2), 44.8 (N-CH_2), 75.5 (d, J = 13.8 Hz), 83.9 (d, J = 11.4 Hz), 110.3, 120.3, 126.2, 131.8, 132.9 (5 × BI-*C*), 133.5, 133.6, 133.7 (3 × Ar-*C*), 136.6 (BI-*C*), 140.1 (N=*C*-N).

Complex 9: Yield: 79%. Elemental analysis: calcd (%) for $C_{29}H_{38}ClN_2Ir$ (642.30): C, 54.23; H, 5.96; N, 4.36%. Found: C, 54.12; H, 5.83; N, 4.17%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 1.59 (m, 4H), 1.92 (m, 4H, COD-CH_2), 2.14–2.42 (s, 15H, Ar-CH_3, 6H, BI-CH_3), 3.17 (br, 2H), 4.39 (br, 2H, COD-C*H*), 5.27 (s, 2H, N-CH_2), 7.21 (s, 1H), 7.34 (s, 1H, BI-*H*), 8.77 (s, 1H, N=C*H*-N). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$) δ: 16.4, 16.5, 16.7 (3 × Ar-*C*H_3), 20.4, 20.6 (2 × BI-*C*H_3), 31.2, 32.4 (2 × COD-*C*H_2), 44.9 (N-*C*H_2), 58.3, 69.0 (2 × COD-*C*H), 110.4, 120.0, 125.9, 131.7, 133.1 (5 × BI-*C*), 133.2, 133.4, 133.7 (3 × Ar-*C*), 136.7 (BI-*C*), 139.6 (N=*C*-N).

Complex 6d′: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.10–2.43 (m, 30H, Ar-CH_3, 12H, BI-CH_3), 5.58 (s, 4H, N-CH_2), 6.39 (s, 2H), 7.89 (s, 2H, BI-*H*), 8.21 (t, 1H, J_1 = 7.6 Hz, J_2 = 8.4 Hz, Py-H_p), 8.52 (d, 2H, J = 7.6 Hz, Py-H_m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.8, 16.9, 17.2 (3 × Ar-*C*H_3), 20.2, 20.8 (2 × BI-*C*H_3), 48.2 (N-*C*H_2), 112.9, 119.2, 127.2 (3 × BI-*C*), 128.6 (Py-C_m), 129.7 (BI-*C*), 132.5, 133.1 (2 × Ar-*C*), 133.4, 134.0 (2 × BI-*C*), 134.9 (Py-C_p), 138.9 (Ar-*C*), 148.2 (Py-C_o), 150.6 (N=*C*-N), 167.0 (Ir-*C*O), 170.8 (Ir-*C*O). IR (cm^{-1}): 2026.24 (C=O).

Complex 9′: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.19–2.46 (s, 15H, Ar-CH_3, 6H, BI-CH_3), 5.31 (s, 2H, N-CH_2), 7.41 (s, 1H), 7.67 (s, 1H, BI-*H*), 7.76 (s, 1H, N=C*H*-N). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.6, 16.9, 17.2 (3 × Ar-*C*H_3), 20.4, 20.6 (2 × BI-*C*H_3), 45.3 (N-*C*H_2), 110.8, 119.1, 125.3, 131.3, 133.4 (5 × BI-*C*), 133.9, 134.4, 134.9 (3 × Ar-*C*), 137.2 (BI-*C*), 139.8 (N=*C*-N), 167.3 (Ir-*C*O), 171.4 (Ir-*C*O). IR (cm^{-1}): 2024.21 (C=O).

General procedures for the synthesis of compounds 10 and 11

These ligands were prepared in the same manner as used for complex **2a** with isophthalic acid (20 mmol) or benzoic acid (40 mmol) and 4,5-dimethylbenzene-1,2-diamine (44 mmol).

Compound 10: Yield: 74%. Elemental analysis: calcd (%) for $C_{24}H_{22}N_4$ (366.46): C, 78.66; H, 6.05; N, 15.29%. Found: C, 78.43; H, 6.16; N, 15.18%. ^{1}H NMR (400 MHz, 303 K, DMSO-d_6) δ: 2.33 (s, 12H, BI-CH_3), 7.37 (s, 4H, BI-*H*), 7.65 (t, 1H, J = 7.2 Hz, Ar-*H*), 8.17 (d, 2H, J = 8.0 Hz, Ar-*H*), 8.96 (s, 1H, Ar-*H*). ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 2.30 (s, 12H, BI-CH_3), 6.99 (t, 1H, J = 8.0 Hz, Ar-*H*), 7.29 (brs, 4H, BI-*H*), 7.76 (d, 2H, J = 7.6 Hz, Ar-*H*), 8.22 (s, 1H, Ar-*H*). ^{13}C NMR (100 MHz, 303 K, DMSO-*d*6) δ: 22.5 (BI-*C*H_3), 115.7 (BI-*C*), 124.7, 127.4, 129.8 (Ar-*C*), 131.1 (BI-*C*), 131.7 (Ar-*C*), 138.7 (BI-*C*), 150.5 (N=*C*-NH).

Compound 11: Yield: 78%. Elemental analysis: calcd (%) for $C_{15}H_{14}N_2$ (222.29): C, 81.05; H, 6.35; N, 12.60%. Found: C, 80.09; H, 6.21; N, 12.43%. ^{1}H NMR (400 MHz, 303 K, DMSO-d_6) δ: 2.30 (s, 6H, BI-CH_3), 7.35 (s, 2H, BI-*H*), 7.44 (m, 1H, Ar-*H*), 7.52 (t, 2H, J = 7.4 Hz, Ar-*H*), 8.15 (d, 2H, J = 6.8 Hz, Ar-*H*). ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 2.35 (s, 6H, BI-CH_3), 7.21 (brs, 1H, BI-*H*), 7.41 (m, 3H, Ar-*H*), 7.52 (brs, 1H, BI-*H*), 8.04 (m, 2H, Ar-*H*). ^{13}C NMR (100 MHz, 303 K, DMSO-*d*6) δ: 20.4 (BI-*C*H_3), 126.7, 129.3, 129.9 (Ar-*C*), 130.9 (BI-*C*), 131.0 (Ar-*C*), 150.8 (N=*C*-NH).

General procedures for the synthesis of complexes 12 and 13

$[M(COD)Cl]_2$ (0.12 mmol) in a dry dichloromethane solution (30 mL) was added under nitrogen to a dichloromethane solution (10 mL) of the ligand (0.24 mmol or 0.12 mmol). The resulting solution was stirred for 24 hours at room temperature; then, the yellow precipitate was filtered off, washed with diethyl ether (20 mL), and dried in a vacuum to obtain the product.

Complex 12: Yield: 73%. Elemental analysis: calcd (%) for $C_{40}H_{46}Cl_2Ir_2N_4$ (1038.16): C, 46.28; H, 4.47; N, 5.40%. Found: C, 46.09; H, 4.56; N, 5.42%. ^{1}H NMR (400 MHz, 303 K, $CDCl_3$) δ: 0.88–1.03 (m, 2H, COD-CH_2), 1.19–1.22 (m, 2H, COD-CH_2), 1.39–1.48 (m, 2H, COD-CH_2), 1.66–1.71 (m, 2H, COD-CH_2), 1.92–2.03 (m, 2H, COD-CH_2), 2.18–2.51 (m, 6H, COD-CH_2, 12H, BI-CH_3, 1H, COD-C*H*), 2.96–2.71 (m, 2H, COD-C*H*), 3.04–3.08 (m, 2H, COD-C*H*), 3.25–3.26 (m, 2H, COD-C*H*), 3.99–4.04 (m, 2H, COD-C*H*), 4.23–4.25 (m, 2H, COD-C*H*), 4.58–4.60 (m, 2H, COD-C*H*), 4.69–4.71 (m, 2H, COD-C*H*), 6.78 (s, 1H, BI-*H*), 7.05 (s, 1H, BI-*H*), 7.52 (t, 1H, J = 7.8, Ar-*H*), 7.52 (d, 1H, J = 7.2, Ar-*H*), 7.85 (s, 1H, BI-*H*), 8.18 (s, 1H, BI-*H*), 9.22 (d, 1H, J = 8.4, Ar-*H*), 9.68 (s, 1H, Ar-*H*), 11.30 (brs, 1H, N*H*), 12.83 (brs, 1H, N*H*).

Complex 13: Yield: 76%. Elemental analysis: calcd (%) for $C_{23}H_{26}ClIrN_2$ (558.14): C, 49.49; H, 4.70; N, 5.02%. Found: C, 49.09; H, 4.73; N, 5.11%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.13–1.17 (m, 1H, COD-CH_2), 1.31–1.42 (m, 3H, COD-CH_2), 2.10 (s, 3H, BI-CH_3), 2.18–2.29 (m, 2H, COD-CH_2), 2.36–2.43 (m, 1H, COD-CH_2, 3H, BI-CH_3), 2.54–2.58 (m, 1H, COD-C*H*), 3.16–3.20 (m, 2H, COD-C*H*), 4.47–4.52 (m, 2H, COD-C*H*),

4.56–4.60 (m, 2H, COD-C*H*), 6.65 (s, 1H, BI-*H*), 7.20 (t, 2H, J = 7.8 Hz, Ar-*H*), 7.26–7.31 (m, 1H, Ar-*H*), 8.06 (s, 1H, BI-*H*), 8.43 (d, 2H, J = 7.6 Hz, Ar-*H*), 11.02 (brs, 1H, N*H*).

General procedure for the TH reactions

A mixture of acetophenone (1 mmol), the catalyst (0.25 mol%), KOH (0.1 mmol), and propan-2-ol (1 mL) was stirred at 82 °C. At the desired reaction times, aliquots were withdrawn from the reaction vessel. The reaction was monitored by ^{1}H-NMR. The conversions were recorded for an average of three runs.

X-Ray crystallography

CCDC 1865637† contains the supplementary crystallographic data for **3d**. A suitable single crystal sample of 0.127 × 0.328 × 0.409 mm^3 was chosen for crystallographic studies, and then placed on the goniometer head of an Agilent X Calibur X-ray diffractometer with an EOS CCD detector. All diffraction measurements were performed at room temperature (25 °C) within the θ range of $3.0 \leq \theta \leq 29.2$, and Mo-$K_\alpha$ (graphite crystal monochromator λ = 0.7107 Å) was used as the radiation source. The absorption correction was based on multiple scans.[28] The crystal structure was solved by direct methods (SHELXS-97).[29] A total of 15 414 reflections were collected for h_{min} = −36, h_{max} = 32, k_{min} = −12, k_{max} = 12, and l_{min} = −18, l_{max} = 29. The refinement of the structure was carried out by the full-matrix least-squares technique on 335 parameters using SHELXL-97,[29] and during this process, 6812 unique reflections (R_{int} = 0.0268) were used. Hydrogen atoms were placed in calculated positions and treated as riding atoms with C–H distances in the range of 0.93–0.97 Å and with U_{iso}(H) values of 1.2U_{eq}(C). ORTEP-3 was used to generate the thermal ellipsoid plots.[30] All geometric calculations and molecular graphics were generated using PLATON software.[31] Further details about the data collection conditions and parameters of the refinement process are presented in Table S1.† The intra-molecular- and intermolecular hydrogen bonding geometries of the title compound are listed in Table S2.†

Conflicts of interest

There are no conflicts to declare.

References

1 (*a*) P. Buchwalter, J. Rosé and P. Braunstein, *Chem. Rev.*, 2015, **115**, 28–126; (*b*) E. K. van den Beuken and B. L. Feringa, *Tetrahedron*, 1998, **54**, 12985–13011.
2 (*a*) J. Park and S. Hong, *Chem. Soc. Rev.*, 2012, **41**, 6931–6943; (*b*) M. Delferro and T. J. Marks, *Chem. Rev.*, 2011, **111**, 2450–2485.
3 (*a*) M. Orbach, S. Shankar, O. V. Zenkina, P. Milko, Y. Diskin-Posner and M. E. van der Boom, *Organometallics*, 2015, **34**, 1098–1106; (*b*) A. L. Gavrilova and B. Bosnich, *Chem. Rev.*, 2004, **104**, 349–384; (*c*) V. Diachenko, M. J. Page, M. R. D. Gatus, M. Bhadbhade and B. A. Messerle, *Organometallics*, 2015, **34**, 4543–4552; (*d*) S. Langbein, H. Wadepohl and L. H. Gade, *Organometallics*, 2016, **35**, 809–815; (*e*) G. Türkmen, A. Atik, Z. S. Şahin and H. Türkmen, *Tetrahedron*, 2015, **71**, 4770–4778; (*f*) S. W. S. Choy, M. J. Page, M. Bhadbhade and B. A. Messerle, *Organometallics*, 2013, **32**, 4726–4729; (*g*) J. H. H. Ho, S. W. S. Choy, S. A. Macgregor and B. A. Messerle, *Organometallics*, 2011, **30**, 5978–5984.
4 (*a*) K. Chan, C. Yik-Sham Chung and V. Wing-Wah Yam, *Chem. Sci.*, 2016, **7**, 2842–2855; (*b*) A. K. W. Chan, D. Wu, K. M. C. Wong and V. W. W. Yam, *Inorg. Chem.*, 2016, **55**, 3685–3691; (*c*) J. Y. Shao and Y. W. Zhong, *Inorg. Chem.*, 2013, **52**, 6464–6472.
5 K. Li, T. Zou, Y. Chen, X. Guan and C. M. Che, *Chem. – Eur. J.*, 2015, **21**, 7441–7453.
6 J. Qian, J. Hu, H. Yoshikawa, J. Zhang, K. Awaga and C. Zhang, *Eur. J. Inorg. Chem.*, 2015, **12**, 2110–2119.
7 A. Y. Y. Tam, W. H. Lam, K. M. C. Wong, N. Zhu and V. W. W. Yam, *Chem. – Eur. J.*, 2008, **14**, 4562–4576.
8 J. Wang, B. Djukic, J. Cao, A. Alberola, F. S. Razavi and M. Pilkington, *Inorg. Chem.*, 2007, **46**, 8560–8568.
9 J. M. Bénech, C. Piguet, G. Bernardinelli, J. C. G. Bünzlic and G. Hopfgartnerd, *J. Chem. Soc., Dalton Trans.*, 2001, **5**, 684–689.
10 (*a*) X. Wang, S. Wang, L. Li, E. B. Sundberg and G. P. Gacho, *Inorg. Chem.*, 2003, **42**, 7799–7808; (*b*) M. Kose and V. McKee, *Polyhedron*, 2014, **75**, 30–39.
11 (*a*) V. G. Vaidyanathan and B. U. Nair, *J. Inorg. Biochem.*, 2002, **91**, 405–412; (*b*) J. Wang, L. Shuai, X. Xiao, Y. Zeng, Z. Li and T. M. Inoue, *J. Inorg. Biochem.*, 2005, **99**, 883–885; (*c*) V. G. Vaidyanathan and B. U. Nair, *Eur. J. Inorg. Chem.*, 2003, **19**, 3633–3638; (*d*) V. G. Vaidyanathan and B. U. Nair, *Dalton Trans.*, 2005, 2842–2848; (*e*) P. Wang, C. H. Leung, D. L. Ma, S. C. Yan and C. M. Che, *Chem. – Eur. J.*, 2010, **16**, 6900–6911.
12 *Modern Reduction Methods*, ed. P. G. Andersson and I. J. Munslow, Wiley-VCH, Weinheim, Germany, 2008.
13 A. Aupoix, C. Bournaud and G. Vo-Thanh, *Eur. J. Org. Chem.*, 2011, 2772–2776.
14 (*a*) T. Ohkuma, H. Ooka, S. Hashiguchi, T. Ikariya and R. Noyori, *J. Am. Chem. Soc.*, 1995, **117**, 10417–10418; (*b*) D. Wang and D. Astruc, *Chem. Rev.*, 2015, **115**, 6621–6686.
15 T. Ikariya and A. J. Blacker, *Acc. Chem. Res.*, 2007, **40**, 1300–1308.
16 S. Günnaz, N. Özdemir, S. Dayan, O. Dayan and B. Çetinkaya, *Organometallics*, 2011, **30**, 4165–4173.
17 (*a*) J. M. Ashley, J. H. Farnaby, N. Hazari, K. E. Kim, E. D. Luzik Jr., R. E. Meehan, E. B. Meyer, N. D. Schley, T. J. Schmeier and A. N. Tailor, *Inorg. Chim. Acta*, 2012, **380**, 399–410; (*b*) R. Maity, S. Hohloch, C.-Y. Su, M. van der Meer and B. Sarkar, *Chem. – Eur. J.*, 2014, **20**, 9952–9961; (*c*) A. Volpe, S. Baldino, C. Tubaro, W. Baratta, M. Basato and C. Graiff, *Eur. J. Inorg. Chem.*, 2016, **2**, 247–251.

18 F. Hildebrand, C. Kohlmann, A. Franz and S. Lütz, *Adv. Synth. Catal.*, 2008, **350**, 909–918.
19 (*a*) H. Türkmen, L. Pelit and B. Çetinkaya, *J. Mol. Catal. A: Chem.*, 2011, **348**, 88–93; (*b*) L. Gök, S. Günnaz, Z. S. Şahin, L. Pelit and H. Türkmen, *J. Organomet. Chem.*, 2017, **827**, 96–104.
20 M. J. Palmer and M. Wills, *Tetrahedron: Asymmetry*, 1999, **10**, 2045–2061.
21 (*a*) H. Türkmen, T. Pape, F. E. Hahn and B. Çetinkaya, *Organometallics*, 2008, **27**, 571–575; (*b*) H. Türkmen, T. Pape, F. E. Hahn and B. Çetinkaya, *Eur. J. Inorg. Chem.*, 2008, 5418–5423.
22 (*a*) M. Ikhile, V. O. Nyamori and M. D. Bala, *Tetrahedron Lett.*, 2012, **53**, 4925–4928; (*b*) D. Gülcemal, A. G. Gökçe, S. Gülcemal and B. Çetinkaya, *RSC Adv.*, 2014, **4**, 26222–26230; (*c*) S. Gülcemal, A. G. Gökce and B. Çetinkaya, *Inorg. Chem.*, 2013, **52**, 10601–10609.
23 E. İnkaya, S. Günnaz, N. Özdemir, O. Dayan, M. Dinçer and B. Çetinkaya, *Spectrochim. Acta, Part A*, 2013, **103**, 255–263.
24 Y. Takenaka and K. Osakada, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 129–130.
25 H. Wu, X. Huang, J. Yuan, J. Ding and R. Yun, *Z. Kristallogr. - New Cryst. Struct.*, 2009, **224**, 419–420.
26 A. W. Addison and P. J. Burke, *J. Heterocycl. Chem.*, 1981, **18**, 803–805.
27 A. W. Van der Made and R. H. Van der Made, *J. Org. Chem.*, 1993, **58**, 1262–1263.
28 *CrysAlisPro Software system (Version 1.171.35.11)*, Agilent Technologies UK Ltd, 2011.
29 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.
30 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565–566.
31 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.