

Synthesis and Reactivities of Cp*Ir Amide and Hydride Complexes Bearing C–N Chelate Ligands

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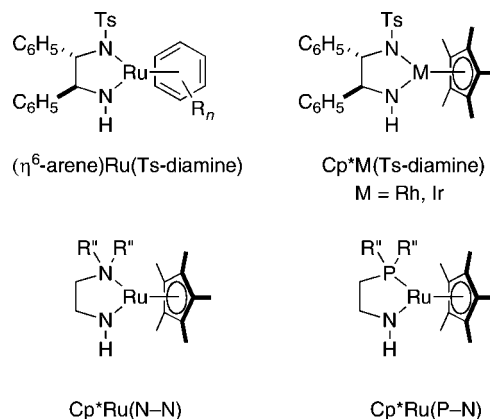
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A series of 16-electron Cp*Ir amide complexes with C–N chelating ligands, Cp*Ir[$\kappa^2(N,C)$ -(NHCR₂-2-C₆H₄)] (**2a**: R = C₆H₅, **2b**: R = CH₃), and the chiral version, Cp*Ir[$\kappa^2(N,C)$ -(R)-{NHCH(CH₃)-2-C₁₀H₆}] (**2e**), were obtained in good to excellent yields from reactions of 18-electron iridium amine complexes, Cp*IrCl[$\kappa^2(N,C)$ -(NH₂CR₂-2-C₆H₄)] (**1a**: R = C₆H₅, **1b**: R = CH₃) and Cp*IrCl[$\kappa^2(N,C)$ -(R)-{NH₂CH(CH₃)-2-C₁₀H₆}] (**1e**), with a base. The amido complexes **2** readily reacted with 2-propanol to convert into hydrido(amine) complexes **3** in almost quantitative yields. The chiral amido complex has proven to serve as an efficient catalyst for asymmetric transfer hydrogenation of acetophenone with 2-propanol, giving 1-phenylethanol with a moderate ee. The Brønsted basicity on the metal–NH moiety in the amido complexes was evaluated by deprotonation of acetic acid, dimethyl malonate, and acetone, leading to the corresponding acetato(amine) complex **4** and alkyl(amine) complexes **5** and **6**, respectively, indicating that the amido–Ir complexes bearing the C–N chelate have more basic properties than those with N-sulfonylated diamine ligands.

Introduction

Much attention has been given to the design of chiral bifunctional molecular catalysts to attain highly efficient molecular transformation for organic synthesis.¹ We have developed chiral transition metal amide complexes, Ru[$\kappa^2(N,N')$ -TsNCHC₆H₅CHC₆H₅NH](η^6 -arene) and Cp*M[$\kappa^2(N,N')$ -TsNCHC₆H₅CHC₆H₅NH] (M = Rh and Ir, Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl, Ts = *p*-toluenesulfonyl), bearing a metal/NH bifunctional moiety as efficient catalysts for the asymmetric reduction of ketones with 2-propanol or formic acid^{1note,2} as well as enantioselective C–C^{1note,3a–e} and C–N bond^{3f} formation. Due to the nature of the metal–N bond, the amido complex smoothly deprotonates the acidic compounds to give the amine complex, which might be a key step in the asymmetric transformation with high efficiency in terms of reactivity and selectivity. We have also shown that changing

Chart 1



the ligand from *N*-sulfonylated diamines (Ts-diamine) to the *N,N*-dimethylaminoethylethylamines (N–N) and 2-phosphinoethylethylamines (P–N) (Chart 1) causes a drastic change in the catalyst performance.⁴ For example, in contrast to the low reactivity of Ru(Ts-diamine)(η^6 -arene) toward H₂ under mild conditions, both Cp*Ru(N–N) and Cp*Ru(P–N) complexes readily activate H₂ with help from protic solvents^{4a,b,d,5} and can efficiently catalyze

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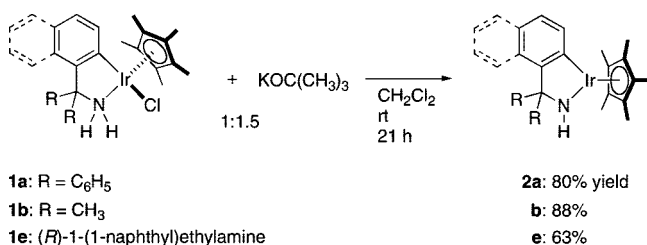
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Scheme 1



the hydrogenation of ketones and epoxides to secondary alcohols. The difference in their reactivity can be attributed to the electronic nature of the metal center induced by the tosylated amido, the tertiary amino, and phosphino groups in the ligands. These results prompted us to explore new catalysts with further modification of the structure of the amine ligands that adjusts the balance of the electronic factors, and we successfully isolated a new type of C–N chelate amido–Ir complexes derived from benzylic amines, Cp*Ir[κ²(N,C)-(NHCR₂-2-C₆H₄)], and their chiral version, Cp*Ir[κ²(N,C)-(R)-{NHCH(CH₃)-2-C₁₀H₆}].

Related cationic transition metal complexes bearing cyclometalated C–N ligands were intensively investigated by Pfeffer and co-workers, but catalytically active amido and hydrido(amine) complexes have not been isolated.⁶ Herein we disclose full details of the synthesis of amido– and hydrido(amine)–Ir complexes bearing C–N ligands and their properties including catalytic activity.

Results and Discussion

Synthesis and Structure of Cyclometalated Amido–Ir Complexes. The cyclometalated amido–Ir complexes Cp*Ir[κ²(N,C)-(NHCR₂-2-C₆H₄)] (**2a**: R = C₆H₅, **2b**: R = CH₃) and Cp*Ir[κ²(N,C)-(R)-{NHCH(CH₃)-2-C₁₀H₆}] (**2e**) were obtained as purple solids in good yields from the reaction of the Ir chloride complexes Cp*IrCl[κ²(N,C)-(NH₂CR₂-2-C₆H₄)] (**1a**: R = C₆H₅, **1b**: R = CH₃) and Cp*IrCl[κ²(N,C)-(R)-{NHCH(CH₃)-2-C₁₀H₆}] (**1e**) with 1.5 equiv of KOC(CH₃)₃ in CH₂Cl₂ at room temperature (Scheme 1). Single-crystal X-ray crystallography of **2a**, illustrated in Figure 1, indicates that **2a** is a monomeric 16-electron neutral complex with a planar geometry around the metal center bearing Cp* and a C–N chelate ligand. The amido complex has a relatively short Ir–N bond, 1.903(2) Å, compared with that of the Ir–NH₂ bond, 2.137 Å, in the chloro complex

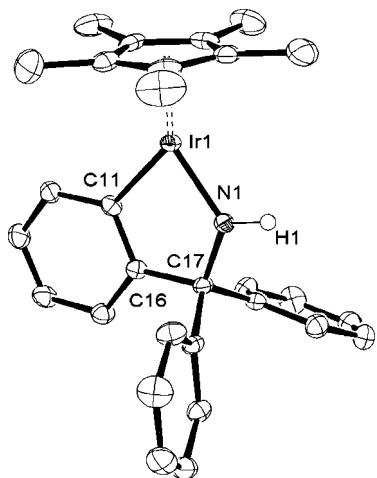


Figure 1. Molecular structure of Cp*Ir[κ²(N,C)-{NHC(C₆H₅)₂-2-C₆H₄}] (**2a**). The hydrogen atoms are omitted for clarity, and the ellipsoids represent 50% probability.

1a (see the Supporting Information), as observed in analogous amido– and (hydrido)amine–Ru complexes.^{2e} The ¹H NMR spectrum of **2a** in CD₂Cl₂ is consistent with its structure in the solid state. The NH signal was observed at 8.00 ppm, which is a lower chemical shift than the NH₂ signals of the parent complex **1a** (4.97 and 5.72 ppm), possibly due to the sp² hybridization at the nitrogen atom. Similarly, ¹H NMR spectroscopic data in the amido complexes **2b** and **2e** display the NH signal at 8.47 and 8.42 ppm, respectively.

The starting neutral chloride complexes **1a** and **1b** were readily prepared from the reaction of [Cp*IrCl₂]₂ and primary benzylamines (C₆H₅CR₂NH₂; R = C₆H₅ and CH₃) in the presence of NaOCOCH₃ in CH₂Cl₂ at room temperature.⁷ The products were fully characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography (see Experimental Section and the Supporting Information). The cycloridation was found to proceed through formation of the monomeric κ¹(N)-amine complex Cp*IrCl₂[κ¹(N)-NH₂CR₂C₆H₅] to give complexes **1a** and **1b**. Notably, the cyclometalation step⁸ was markedly accelerated in the presence of sodium acetate, suggesting that the Ir acetate species acts as a key intermediate for the electrophilic activation of a C–H bond of the aromatic group, as observed by Davies⁹ and us.¹⁰ In fact, an isolable bis(acetato)–Ir complex, Cp*Ir(OCOCH₃)₂, readily reacted with triphenylmethylaniline without any additives to give the corresponding cyclometalated Ir complex **4**, with the acetato ligand, determined by X-ray crystallography and NMR spectroscopy (*vide infra*). Similarly, we obtained the cyclometalated complexes **1c** (R = H, CH₃), **1d** (R = H, H), **1e**, and **1f** (R = H, CH₂OSi(CH₃)₂tBu), bearing sterically less hindered amines with good yields and selectivities, although the reaction required a higher reaction temperature of 60 °C in CH₃CN. These results imply that the substituents on the α-carbon bound to the NH₂ group significantly influence the rate of the cyclometalation.

Synthesis and Reactivities of Cyclometalated Hydrido–Ir Complexes. The isolable 16-electron amido complex **2a** was found to react readily with 2-propanol at ambient temperature, leading to the 18-electron hydrido(amine) complex Cp*IrH[κ²(N,C)-{NH₂C(C₆H₅)₂-2-C₆H₄}] (**3a**) in 88% yield (Scheme 2), as previously observed in Ru– and Ir–Ts-diamine complexes.^{2e,g} Similarly, the amido complex **2b** was readily converted to the hydrido complex **3b**. The IR spectra of **3a** and **3b** display Ir–H stretching frequencies at 2024 and 2064 cm^{−1}, respectively. The ¹H NMR spectra of **3a** and **3b** in CD₂Cl₂ show hydride signals at −12.9 and −13.2 ppm, respectively, in addition to two broad peaks due to NH protons at 4.33 and 5.78 ppm for **3a** and at 3.21 and 4.47 ppm for **3b**.

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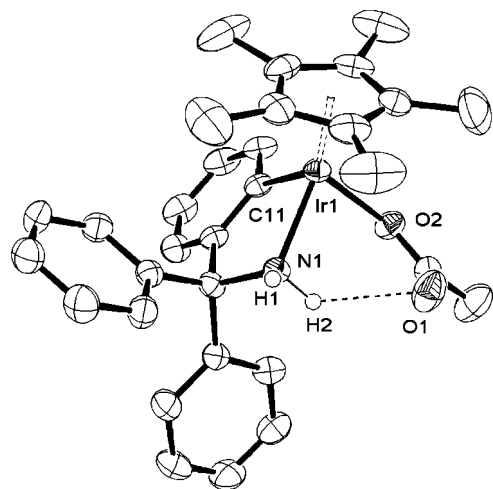
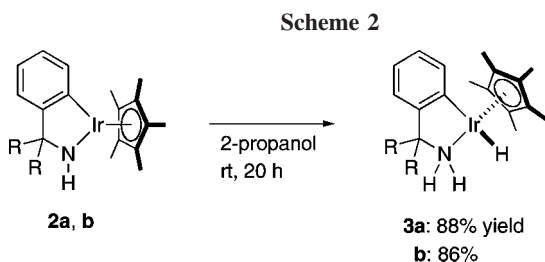


Figure 2. Molecular structure of $\text{Cp}^*\text{Ir}(\text{OCOCH}_3)[\kappa^2(\text{N,C})\{-\text{NH}_2\text{C}(\text{C}_6\text{H}_5)_2\text{-2-C}_6\text{H}_4\}]$ (**4**). Ellipsoids are shown at the 50% probability level for the non-hydrogen atoms. The dashed line indicates the hydrogen bond.

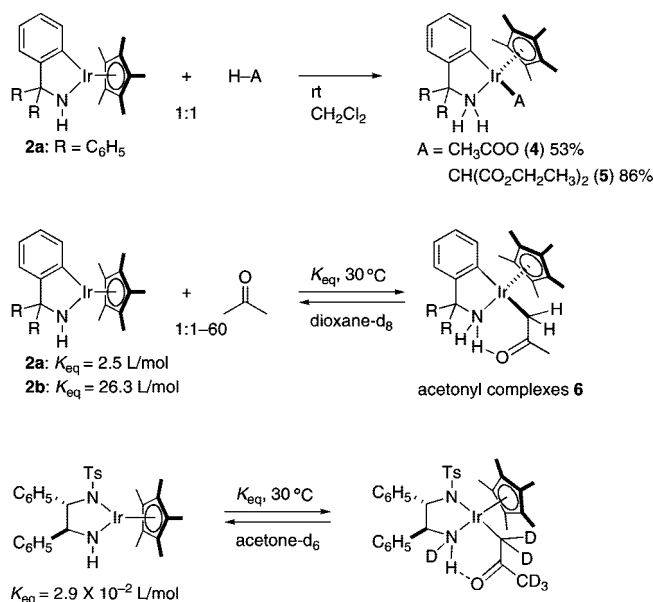


These hydrido complexes were found to be thermally stable under an Ar atmosphere. Thermal treatment of the 18-electron deuterio(amine) complex **3b-D** in 1,4-dioxane at 100 °C provided no deuterio scrambling on this complex, indicating that neither reductive elimination of the hydrido ligand and phenyl fragment on the C–N chelate ligand followed by recyclometalation of the $\kappa^1(\text{N})$ -amine complex nor an exchange reaction between the hydrido ligand and coordinated amine protons took place. Notably, the isolable hydrido complexes have proven to react with oxygen under mild conditions, providing the corresponding amido complexes.¹¹

The hydrido complex **3a** reacted smoothly with acetone (in a mole ratio of 12 based on **3a**) in CH_2Cl_2 at room temperature to give 2-propanol, while it did not react with olefins such as styrene, under identical conditions, due to the coordinatively saturated structure of the hydrido(amine) complex, as observed in analogous bifunctional catalysts.¹² The hydrogen atoms in the hydrido(amine) complex transfer to acetone possibly through a six-membered pericyclic transition state as previously proposed.¹³

Reactivities of Cyclometalated Amido–Ir Complexes as Brønsted Bases. Thanks to the nature of the Ir–NH group, the amido–Ir complex readily reacted with acidic compounds

Scheme 3



via deprotonation as shown in Scheme 3 and as observed in the related amido–Ru complexes.^{3a,14} The reaction of **2a** with 1 equiv of acetic acid ($\text{p}K_a$ in DMSO = 12.3)¹⁵ in CH_2Cl_2 at room temperature gave the corresponding acetato complex **4**, $\text{Cp}^*\text{Ir}(\text{OCOCH}_3)[\kappa^2(\text{N,C})\{-\text{NH}_2\text{C}(\text{C}_6\text{H}_5)_2\text{-2-C}_6\text{H}_4\}]$, which was also obtained from the cyclometalation of $\text{Cp}^*\text{Ir}(\text{OCOCH}_3)_2$ with triphenylmethylamine, as mentioned above. As shown in Figure 2, the molecular structure of **4**, confirmed by X-ray crystallography, showed that there is a short $\text{N}(\text{H}_2) \cdots \text{O}=\text{C}$ distance of 2.945(3) Å, indicating the presence of an intramolecular hydrogen bond, as observed in the analogous complexes.^{14,16} The $\text{N}(\text{H}) \cdots \text{O}=\text{C}$ interaction in **4** was further evidenced by a significant downfield shift of one of the NH_2 signals at 8.51 ppm in the ^1H NMR spectrum.

Similarly, complex **2a** deprotonated dimethyl malonate ($\text{p}K_a$ in DMSO = 15.9)¹⁵ to give the corresponding C-bound malonato complex **5**, $\text{Cp}^*\text{Ir}[\text{CH}(\text{COOCH}_3)_2][\kappa^2(\text{N,C})\{-\text{NH}_2\text{C}(\text{C}_6\text{H}_5)_2\text{-2-C}_6\text{H}_4\}]$, in 86% yield, as observed in the isolable Ru complex.^{3b} The $^{13}\text{C}\{^1\text{H}\}$ NMR of **5** in CD_2Cl_2 displayed characteristic $\text{C}=\text{O}$ signals of $\text{CH}(\text{COOCH}_3)_2$ at 175.3 and 177.7 ppm. The deprotonation by the amido–Ir complex **2** was also observed for less acidic acetone ($\text{p}K_a$ in DMSO = 26.5).¹⁵ When an acetone solution (1.0×10^{-2} M) of **2a** was stirred at room temperature, the acetonyl(amine) complex **6a**, $\text{Cp}^*\text{Ir}(\text{CH}_2\text{COCH}_3)[\kappa^2(\text{N,C})\{-\text{NH}_2\text{C}(\text{C}_6\text{H}_5)_2\text{-2-C}_6\text{H}_4\}]$, was obtained as an orange solid in 87% yield. The ^1H NMR spectrum in CD_2Cl_2 exhibits two doublet signals assigned to the diastereotopic CH_2 protons of the acetonyl ligand at 2.27 and 3.00 ppm with $^2J_{\text{HH}} = 5.9$ Hz and two distinct signals due to NH protons at 4.40 and 6.80 ppm. Because the presence of the $\text{C}=\text{O}$ moiety was confirmed by a $^{13}\text{C}\{^1\text{H}\}$ NMR signal observed at 213.8 ppm and a CO stretching band at 1596 cm^{-1} in the IR spectrum, we conclude that the acetonyl ligand coordinates to the Ir center in a C-bound mode, as observed in the $\text{Cp}^*\text{Ir}(\text{CH}_2\text{COCH}_3)(\text{Tsdpen})$ (dpn = 1,2-diphenylethylenediamine) complex. Similar spectroscopic features were observed for the related acetonyl(amine)

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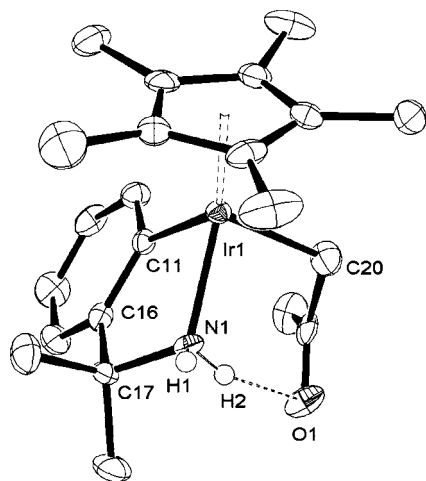


Figure 3. Molecular structure of $\text{Cp}^*\text{Ir}(\text{CH}_2\text{COCH}_3)[\kappa^2(\text{N},\text{C})\{-\text{NH}_2\text{C}(\text{CH}_3)_2\text{-2-C}_6\text{H}_4\}]$ (**6b**). Only one of the two independent molecules is shown. Ellipsoids are shown at the 50% probability level for the non-hydrogen atoms. The dashed line indicates the hydrogen bond.

complex **6b**, $\text{Cp}^*\text{Ir}(\text{CH}_2\text{COCH}_3)[\kappa^2(\text{N},\text{C})\{-\text{NH}_2\text{C}(\text{CH}_3)_2\text{-2-C}_6\text{H}_4\}]$, which was prepared by treatment of **2b** with an excess amount of acetone in 81% yield. The structure of the C-bound acetyl complex was also confirmed by X-ray crystallography of **6b** depicted in Figure 3. An average distance of 2.824 Å for the $\text{N}(\text{H}_2)\cdots\text{O}=\text{C}$ motif indicates the presence of intramolecular hydrogen bonding.

Notably, the acetyl complexes **6** proved to be labile in solution and gradually converted into the amido complexes **2** and free acetone at room temperature. The thermodynamics of the reversible process between the acetyl complex and the amido complex plus acetone indicate that the electronic properties of the chelating ligands delicately affect the basicity of the amido complex. An equilibrium constant (K_{eq}) determined from the ^1H NMR monitoring of the reaction of **2a** with 60 equiv of acetone in dioxane- d_8 at 30 °C was 2.5 L/mol. In contrast, treatment of complex **2b**, having a more electron-donating ligand, with an equimolar amount of acetone at 30 °C gave a K_{eq} value of 26.3 L/mol. These results are consistent with the result obtained with the electron-withdrawing *N*-sulfonylamido complex $\text{Cp}^*\text{Ir}[\kappa^2(\text{N},\text{N}')\text{-TsNCHC}_6\text{H}_5\text{CHC}_6\text{H}_5\text{NH}]$, having $K_{\text{eq}} = 2.9 \times 10^{-2}$ L/mol in an acetone- d_6 solution with a concentration of 0.014 mol/L, as shown in Scheme 3. From the K_{eq} values for **2a** in a temperature range of 30 to 60 °C, the van't Hoff plots can be fit linearly to determine $\Delta H = -53.1$ kJ mol $^{-1}$ and $\Delta S = -173$ J mol $^{-1}$ K $^{-1}$ (see Supporting Information).

Evaluation of Electronic Properties of the Cyclometalated Complexes. As discussed in the previous section, the reactivity of the amido complexes was significantly influenced by a change in the amine ligands. In order to gain further insight into the difference in the electronic properties on the C–N and Ts-diamine ligands, we prepared cationic $\text{Cp}^*\text{Ir}\text{-CO}$ complexes bearing various chelating primary amine ligands.^{4b,17} The cationic carbonyl complexes **7**, with the C–N chelating ligands, were prepared as crystalline compounds from the reaction of **1** with an equimolar amount of AgBF_4 in CH_3CN , followed by exposure to atmospheric pressure of CO in CH_2Cl_2 . The related $\text{Cp}^*\text{Ir}(\text{Tscydn})\text{CO}$ complex **8** (cydn = 1,2-cyclohexanediamine) was similarly obtained. The molecular structure of the isolable

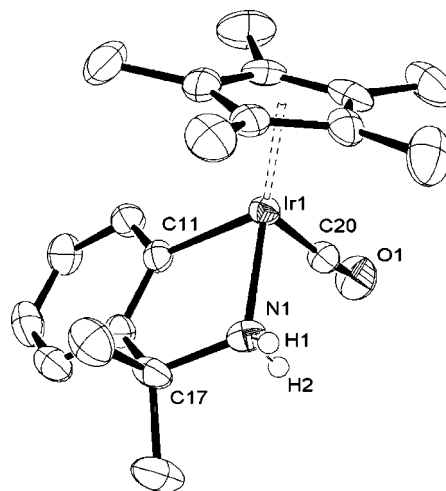
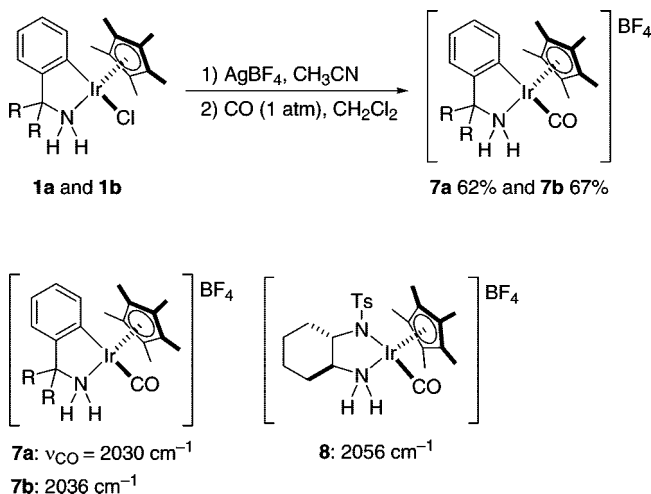


Figure 4. Molecular structure of $[\text{Cp}^*\text{Ir}\{\kappa^2(\text{N},\text{C})\{-\text{NH}_2\text{C}(\text{CH}_3)_2\text{-2-C}_6\text{H}_4\}}(\text{CO})]\text{BF}_4$ (**7b**). Ellipsoids are shown at the 50% probability level for the non-hydrogen atoms.

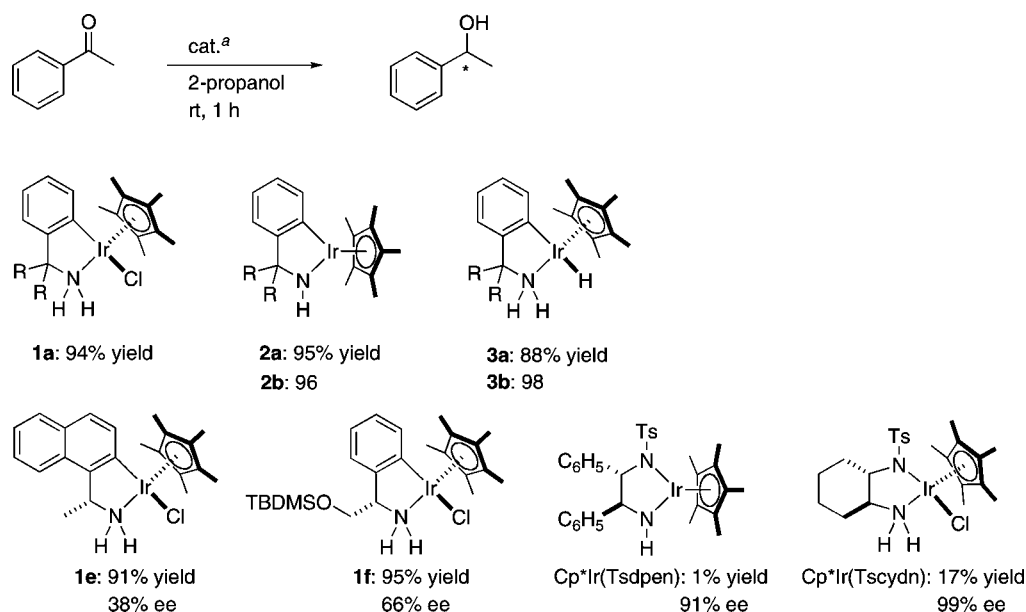
Scheme 4



carbonyl complex **7b**, $[\text{Cp}^*\text{Ir}\{\kappa^2(\text{N},\text{C})\{-\text{NH}_2\text{C}(\text{CH}_3)_2\text{-2-C}_6\text{H}_4\}}(\text{CO})]\text{BF}_4$, shown in Figure 4, confirmed that it has a three-legged piano stool configuration around the metal center and an Ir–CO distance of 1.855(3) Å.

The IR spectra of complexes **7a** and **7b** show the characteristic stretching band of the CO ligand at 2030 and 2036 cm $^{-1}$, respectively. The C–O stretching frequency in the carbonyl complexes increases in the order **7a** $\approx$ **7b** < **8** as shown in Scheme 4, indicating the relatively electron-donating nature of the Ir center with C–N chelate ligands compared to that with Ts-cydn. This trend in the electron-donating properties is consistent with the above-mentioned strong basicity of the amido complexes with C–N ligands.

Catalytic Activity of Both Amido and Hydrido(amine) Complexes. On the basis of detailed structural analysis and reactivities of isolable amido complexes **2** and hydrido(amine) complexes **3** discussed above, we examined catalytic transfer hydrogenation with both complexes. The transfer hydrogenation of acetophenone in 2-propanol containing **2a** or **2b** (substrate/catalyst = 100/1) at room temperature proceeded efficiently to give 1-phenylethanol in 95–96% yield after 1 h. The hydrido(amine) complexes **3a** and **3b** also afforded 1-phenylethanol in comparable yields of 98% and 88%, respectively. The catalytic activity of **2** was found to be much higher than that of

Scheme 5^a

^a Catalysts **1** and Cp*Ir(Tsdydn) required 1.2 equiv of KOC(CH₃)₃ to catalyst.

Cp*Ir(Ts-diamine) complexes (1% yield, 91% ee for the (*S,S*)-Tsdpen complex and 17% yield, 99% ee for the (*S,S*)-Tsdydn complex) under the same conditions. Asymmetric reduction of acetophenone with the chiral Cp*Ir(C–N) complexes **1e** and **1f**, derived from (*R*)-1-(1-naphthyl)ethylamine and (*S*)-2-*tert*-butyldimethylsiloxy-1-phenylethylamine, in the presence of KOC(CH₃)₃ gave (*S*)-1-phenylethanol in 91–95% yield albeit with moderate ee (38–66%). These results indicate that amido–Ir complexes with C–N chelating ligands could be promising bifunctional catalysts for highly efficient transfer hydrogenation, although fine-tuning of the chiral ligands might be required for improvement in the enantioselectivity.

Conclusions

We isolated and characterized 16-electron cyclometalated amido–Ir complexes **2** having the metal/NH bifunctionality. These amido complexes **2** were readily converted into the isolable hydrido(amine) complexes **3** in 2-propanol, and the reverse hydrogen transfer from **3** to acetone was also demonstrated. Because of the reversibility between **2** and **3**, the C–N chelate Ir complexes were successfully applied to catalytic transfer hydrogenation of acetophenone, which showed greater activity than the Cp*Ir(Ts-diamine) catalyst system. Due to a relatively stronger basicity originating from the nature of the amido complexes with the C–N ligand, they reacted smoothly with acidic compounds such as acetic acid, dimethyl malonate, and acetone to give the corresponding amine Ir complexes **4–6**. The basicity of the amido complexes was highly influenced by the modification of the chelating amine ligands, as shown by the equilibrium constants for the deprotonation of acetone. IR analysis of the carbonyl complexes **7** and **8** also provides good evidence for enhancement of the σ -donor capability of the C–N chelating ligands, compared to the Ts-diamine chelating ligand. The present work indicates that the C–N ligands allow one to modulate the electronic properties of the metal/NH bifunctional systems, leading to high catalytic performance. Now we are working on the development of new catalysis based on the reactivity of these C–N complexes.

Experimental Section

General Procedures. All experiments were conducted under an argon atmosphere using Schlenk techniques. All deuterated NMR solvents were dried and degassed by appropriate methods. Solvents were purchased from Kanto Chemical and dried by refluxing over sodium benzophenone ketyl (THF, toluene, diethyl ether), P₂O₅ (dichloromethane, hexane, acetonitrile), or CaSO₄ (acetone) and distilled under argon. [Cp*IrCl₂]₂,¹⁸ Cp*Ir(OCOCH₃)₂,¹⁹ (*S*)-2-*tert*-butyldimethylsiloxy-1-phenylethylamine,²⁰ Cp*Ir[κ^2 (*N,N'*)-(S,S)-TsNCHC₆H₅CHC₆H₅NH],²⁸ and Cp*IrCl[κ^2 (*N,N'*)-(S,S)-Tsdydn]²⁸ were prepared according to the literature. A deuterated alcohol, 3-pentanol-*d*₁, was prepared by reduction of 3-pentanone with NaBD₄. Other reagents were used as delivered. ¹H and ¹³C{¹H} NMR spectra were recorded on a JEOL JNM-LA300 spectrometer and referenced to SiMe₄ via the solvent resonance. Elemental analyses were carried out using a PE2400 Series II CHNS/O analyzer (Perkin-Elmer). IR spectra were recorded on a JASCO FT/IR-610 spectrometer.

The experimental and analytical procedures for catalytic transfer hydrogenation were performed according to the literature.²⁸ Analytical gas chromatography was performed with a Shimadzu GC-17A gas chromatograph equipped with an Inert Cap Wax capillary column (0.25 mm $\times$ 30 m) purchased from GL Sciences Inc. Analytical chiral HPLC was performed on a Chiralcel OD column (4.6 mm $\times$ 25 cm) purchased from Daicel Chemical Industries, Ltd.

General Procedure for Synthesis of Cp*IrCl[κ^2 (*N,C*)-(NH₂CR₂-2-C₆H₄)] (1a**: R = C₆H₅, **1b**: R = CH₃). A mixture of [Cp*IrCl₂]₂ (0.1 g, 0.13 mmol), the appropriate benzylamine (0.25 mmol), and NaOAc (0.027 g, 0.33 mmol) in CH₂Cl₂ (5 mL) was stirred at room temperature for 20 h. The solvent was removed under reduced pressure. After the reaction mixture in toluene was filtered through filter paper, evaporation of the filtrate to dryness gave the iridacycle product.**

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Cp*IrCl[$\kappa^2(N,C)$ -(NH₂C(C₆H₅)₂-2-C₆H₄)] (1a). Orange crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into the solution in CH₂Cl₂. Isolated yield: 76% (0.105 g, 0.17 mmol). ¹H NMR (300.4 MHz, CD₂Cl₂, rt, δ /ppm): 1.39 (s, 15H; C(CH₃)₅), 4.97, 5.72 (each d, ²J_{HH} = 10 Hz, 1H; NH₂C(C₆H₅)₂C₆H₄), 6.22–7.58 (m, 14H; NH₂C(C₆H₅)₂C₆H₄). ¹³C{¹H} NMR (75.6 MHz, CD₂Cl₂, rt, δ /ppm): 8.4 (C₅(CH₃)₅), 80.5 (NH₂C(C₆H₅)₂C₆H₄), 88.4 (C₅(CH₃)₅), 121.4, 125.9, 127.2, 128.0, 128.4, 128.5, 129.6, 129.7, 137.0, 147.6, 148.1, 152.3, 152.4, 152.6 (NH₂C(C₆H₅)₂C₆H₄). IR (cm⁻¹, KBr): 3280 (w), 3232 (w), 3045 (w), 2983 (w), 2959 (w), 2913 (w), 1570 (m), 1493 (m), 1445 (m), 1034 (m), 702 (m). Anal. Calcd for C₂₉H₃₁NClIr(CH₂Cl₂)_{0.5}: C 53.39, H 4.86, N 2.11. Found: C 53.50, H 4.92, N 2.09.

Cp*IrCl[$\kappa^2(N,C)$ -(NH₂C(CH₃)₂-2-C₆H₄)] (1b). Orange crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into the solution in CH₂Cl₂. Isolated yield: 79% (0.095 g, 0.19 mmol). ¹H NMR (300.4 MHz, CDCl₃, rt, δ /ppm): 1.21, 1.56 (each s, 3H; NH₂C(CH₃)₂C₆H₄), 1.70 (s, 15H; C(CH₃)₅), 3.88, 4.40 (each br, 1H; NH₂C(CH₃)₂C₆H₄), 6.79–6.86 (m, 2H; NH₂C(CH₃)₂C₆H₄), 6.91–6.97 (m, 1H; NH₂C(CH₃)₂C₆H₄), 7.42–7.45 (m, 1H; NH₂C(CH₃)₂C₆H₄). ¹³C{¹H} NMR (75.6 MHz, CDCl₃, rt, δ /ppm): 9.5 (C₅(CH₃)₅), 30.9, 32.0 (NH₂C(CH₃)₂C₆H₄), 66.5 (NH₂C(CH₃)₂C₆H₄), 87.0 (C₅(CH₃)₅), 121.4, 125.6, 127.1, 138.0, 154.2, 155.2 (NH₂C(CH₃)₂C₆H₄). IR (cm⁻¹, KBr): 3260 (m), 3219 (m), 2973 (w), 2911 (w), 1577 (m), 1450 (m), 1024 (m), 764 (m), 740 (m). Anal. Calcd for C₁₉H₂₇NClIr: C 45.91, H 5.47, N 2.82. Found: C 46.00, H 5.53, N 2.84.

General Procedure for Synthesis of Cp*IrCl[$\kappa^2(N,C)$ -(NH₂CHR-2-Ar)] (1c: R = CH₃, 1d: R = H, 1e: (R)-1-(1-naphthyl)ethylamine, and 1f: (S)-2-tert-butylidimethylsiloxy-1-phenylethylamine). A mixture of [Cp*IrCl₂]₂ (0.1 g, 0.13 mmol), the appropriate benzylamine (0.25 mmol), and NaOAc (0.027 g, 0.33 mmol) in CH₃CN (5 mL) was stirred at 60 °C for 20 h. The solvent was removed under reduced pressure. After the reaction mixture in toluene was filtered through filter paper, evaporation of the filtrate to dryness gave the iridacycle product.

Cp*IrCl[$\kappa^2(N,C)$ -(NH₂CH(CH₃)-2-C₆H₄)] (1c). Recrystallization from toluene and hexane afforded orange crystals in 34% yield (0.083 g, 0.17 mmol) as a 5:2 mixture of diastereomers. ¹H NMR (300.4 MHz, CDCl₃, rt, δ /ppm): major diastereomer, 1.54 (d, ³J_{HH} = 6.6 Hz, 1H; NH₂CH(CH₃)C₆H₄), 1.72 (s, 15H; C(CH₃)₅), 3.87 (m, 1H; NH₂CH(CH₃)C₆H₄), 3.77, 4.16 (each br, 1H; NH₂CH(CH₃)C₆H₄), 6.80–7.51 (4H; NH₂CH(CH₃)C₆H₄); minor diastereomer, 1.22 (d, ³J_{HH} = 6.6 Hz, 1H; NH₂CH(CH₃)C₆H₄), 1.72 (s, 15H; C(CH₃)₅), 4.34 (m, 1H; NH₂CH(CH₃)C₆H₄), 3.51, 4.72 (each br, 1H; NH₂CH(CH₃)C₆H₄), 6.80–7.18 (m, 4H; NH₂CH(CH₃)C₆H₄). ¹³C{¹H} NMR (75.6 MHz, CDCl₃, rt, δ /ppm): major diastereomer, 9.3 (C₅(CH₃)₅), 22.8 (NH₂CH(CH₃)C₆H₄), 61.8 (NH₂CH(CH₃)C₆H₄), 86.4 (C₅(CH₃)₅), 121.3, 122.4, 127.7, 128.2, 129.0, 136.6 (NH₂CH(CH₃)C₆H₄); minor diastereomer, 9.4 (C₅(CH₃)₅), 24.7 (NH₂CH(CH₃)C₆H₄), 61.2 (NH₂CH(CH₃)C₆H₄), 86.6 (C₅(CH₃)₅), 119.2, 120.1, 125.3, 131.7, 136.2, 137.2 (NH₂CH(CH₃)C₆H₄). IR (cm⁻¹, KBr): 3265 (m), 3213 (m), 3047 (w), 2978 (w), 2910 (w), 1579 (m), 1451 (m), 1378 (w), 1026 (m), 741 (m). Anal. Calcd for C₁₈H₂₅NClIr: C 44.75, H 5.22, N 2.90. Found: C 44.72, H 5.51, N 2.65.

Cp*IrCl[$\kappa^2(N,C)$ -(NH₂CH₂-2-C₆H₄)] (1d). Recrystallization from toluene and hexane afforded orange crystals. Isolated yield: 50% (0.092 g, 0.20 mmol). ¹H NMR (300.4 MHz, CDCl₃, rt, δ /ppm): 1.71 (s, 15H; C(CH₃)₅), 3.75–4.18 (4H; NH₂CH₂C₆H₄), 6.80–7.50 (m, 4H; NH₂CH₂C₆H₄). ¹³C{¹H} NMR (75.6 MHz, CDCl₃, rt, δ /ppm): 9.27 (C₅(CH₃)₅), 55.9 (NH₂CH₂C₆H₄), 86.4 (C₅(CH₃)₅), 120.1, 122.3, 127.2, 136.4, 146.5, 156.8 (NH₂CH₂C₆H₄). IR (cm⁻¹, KBr): 3234 (m), 3136 (w), 3051 (w), 2983 (w), 2910 (m), 1580 (m), 1451 (m), 1367 (w), 1135 (m). Anal. Calcd for C₁₇H₂₃NClIr: C 43.53, H 4.94, N 2.99. Found: C 43.17, H 4.93, N 2.95.

Cp*IrCl[$\kappa^2(N,C)$ -(R)-{NH₂CH(CH₃)-2-C₁₀H₆}] (1e). Recrystallization from toluene and hexane afforded orange crystals. Isolated yield: 31% (0.047 g, 0.087 mmol). ¹H NMR (300.4 MHz, CD₂Cl₂, rt, δ /ppm): 1.54 (d, ³J_{HH} = 7.5 Hz, 3H; NH₂CH(CH₃)C₁₀H₆), 1.62 (s, 15H; C(CH₃)₅), 2.12 (m, 1H; NH₂CH(CH₃)C₁₀H₆), 3.69, 4.82 (each br, 1H; NH₂CH(CH₃)C₁₀H₆), 7.14–7.76 (m, 6H; NH₂-CH(CH₃)C₁₀H₆). ¹³C{¹H} NMR (75.6 MHz, CD₂Cl₂, rt, δ /ppm): 9.6 (C₅(CH₃)₅), 22.7 (NH₂CH(CH₃)C₁₀H₆), 59.7 (NH₂CH(CH₃)C₁₀H₆), 87.2 (C₅(CH₃)₅), 122.9, 123.7, 125.6, 126.2, 128.6, 131.4, 136.5, 146.0, 153.9 (NH₂CH(CH₃)C₁₀H₆). IR (cm⁻¹, KBr): 3273 (m), 3221 (m), 2954 (m), 2928 (m), 1571 (m), 1257 (m), 1247 (m), 1102 (m), 1091 (m), 731 (m). Anal. Calcd for C₂₂H₂₇NClIr(C₆H₅CH₃)_{0.1}: C 50.27, H 5.17, N 2.58. Found: C 50.07, H 5.21, N 2.20.

Cp*IrCl[$\kappa^2(N,C)$ -(S)-{NH₂CH(CH₂OSi(CH₃)₂Bu)-2-C₆H₄}] (1f). Recrystallization from diethyl ether afforded orange crystals. Isolated yield: 35% (0.25 g, 0.4 mmol). ¹H NMR (300.4 MHz, CD₂Cl₂, rt, δ /ppm): 0.12, 0.16 (each s, 3H; OSi(CH₃)₂C(CH₃)₃), 0.75 (s, 9H; OSi(CH₃)₂C(CH₃)₃), 1.72 (s, 15H; C(CH₃)₅), 3.03 (m, 1H; NH₂CH), 3.64, 4.13 (each m, 1H; CH₂), 4.39, 4.71 (each br, 1H; NH₂), 6.78–7.46 (m, 4H; C₆H₄). ¹³C{¹H} NMR (75.6 MHz, CD₂Cl₂, rt, δ /ppm): 8.5 (C(CH₃)₅), 9.3 (C₅(CH₃)₅), 18.3 (OSi(CH₃)₂C(CH₃)₃), 26.0 (C(CH₃)₃), 65.7 (CH₂), 68.3 (NH₂CH), 87.0 (C₅(CH₃)₅), 120.9, 122.3, 127.4, 137.2, 148.4, 156.5 (C₆H₄). IR (cm⁻¹, KBr): 3334 (m), 3042 (m), 3028 (m), 2924 (m), 2909 (m), 2866 (m), 2817 (m), 1611 (m), 1381 (m), 1029 (m). Anal. Calcd for C₂₄H₃₉NOCliIrSi: C 47.00, H 6.41, N 2.28. Found: C 46.85, H 6.53, N 2.33.

General Procedure for Synthesis of Cp*Ir[$\kappa^2(N,C)$ -(NHCR₂-2-Ar)] (2a: R = C₆H₅, 2b: R = CH₃, and 2c: (R)-1-(1-naphthyl)ethylamine). A mixture of Cp*IrCl[$\kappa^2(N,C)$ -(NH₂CR₂-2-Ar)] (0.35 mmol) and dry KOC(CH₃)₃ (0.53 mmol) in CH₂Cl₂ (9 mL) was stirred at room temperature for 21 h. The solvent was removed under reduced pressure. After the residue was dissolved in diethyl ether, insoluble material was removed by filtration. Evaporation to dryness of the filtrate gave the product.

Cp*Ir[$\kappa^2(N,C)$ -(NHC(C₆H₅)₂-2-C₆H₄)] (2a). Recrystallization from a concentrated solution in diethyl ether afforded purple crystals. Isolated yield: 80% (0.16 g, 0.28 mmol). ¹H NMR (300.4 MHz, CD₂Cl₂, rt, δ /ppm): 1.95 (s, 15H; C(CH₃)₅), 6.81–8.09 (m, 14H; NHC(C₆H₅)₂C₆H₄), 8.00 (br, 1H; NHC(C₆H₅)₂C₆H₄). ¹³C{¹H} NMR (75.6 MHz, CD₂Cl₂, rt, δ /ppm): 10.0 (C₅(CH₃)₅), 87.3 (NHC(C₆H₅)₂C₆H₄), 90.9 (C₅(CH₃)₅), 122.6, 124.3, 125.0, 126.3, 127.6, 127.8, 136.8, 145.4, 160.7, 164.5 (NHC(C₆H₅)₂C₆H₄). IR (cm⁻¹, KBr): 3056 (w), 1488 (m), 1442 (m), 1370 (w), 1079 (w), 1026 (m), 779 (m), 727 (m), 696 (m), 636 (m). Anal. Calcd for C₂₉H₃₀NIr: C 59.56, H 5.17, N 2.40. Found: C 59.53, H 5.36, N 2.05.

Cp*Ir[$\kappa^2(N,C)$ -(NHC(CH₃)₂-2-C₆H₄)] (2b). Recrystallization from a concentrated solution in diethyl ether afforded purple crystals. Isolated yield: 88% (0.10 g, 0.22 mmol). ¹H NMR (300.4 MHz, CD₂Cl₂, rt, δ /ppm): 1.32 (s, 6H; NHC(CH₃)₂C₆H₄), 1.94 (s, 15H; C(CH₃)₅), 6.82–6.96 (m, 2H; NHC(CH₃)₂C₆H₄), 7.13 (d, ³J_{HH} = 7.3 Hz, 1H; NHC(CH₃)₂C₆H₄), 8.02 (d, ³J_{HH} = 7.3 Hz, 1H; NHC(CH₃)₂C₆H₄), 8.47 (br, 1H; NHC(CH₃)₂C₆H₄). ¹³C{¹H} NMR (75.6 MHz, CD₂Cl₂, rt, δ /ppm): 10.4 (C₅(CH₃)₅), 27.9 (NHC(CH₃)₂C₆H₄), 78.9 (NHC(CH₃)₂C₆H₄), 87.1 (C₅(CH₃)₅), 120.8, 122.6, 125.1, 136.8, 162.1, 163.3 (NHC(CH₃)₂C₆H₄). IR (cm⁻¹, KBr): 3042 (w), 2964 (m), 2911 (m), 1576 (m), 1428 (m), 1381 (m), 1261 (m), 1099 (m), 1025 (m), 802 (m). Anal. Calcd for C₁₉H₂₆NIr: C 49.54, H 5.69, N 3.04. Found: C 49.45, H 5.72, N 2.92.

Cp*Ir[$\kappa^2(N,C)$ -(R)-{NHCH(CH₃)-2-C₁₀H₆}] (2e). Recrystallization from diethyl ether afforded purple crystals. Isolated yield: 63% (0.083 g, 0.17 mmol). ¹H NMR (300.4 MHz, CD₂Cl₂, rt, δ /ppm): 1.48 (d, ³J_{HH} = 4.5 Hz, 3H; NHCH(CH₃)C₁₀H₆), 1.97 (s, 15H; C(CH₃)₅), 2.91 (m, 1H; NHCH(CH₃)C₁₀H₆), 7.22–8.28 (m, 6H; NHCH(CH₃)C₁₀H₆), 8.42 (br, 1H; NHCH(CH₃)C₁₀H₆). ¹³C{¹H} NMR (75.6 MHz, CD₂Cl₂, rt, δ /ppm): 9.5 (C₅(CH₃)₅), 21.8 (NHCH(CH₃)C₁₀H₆), 74.5 (NHCH(CH₃)C₁₀H₆), 87.7 (C₅(CH₃)₅),

123.1, 124.6, 125.2, 125.3, 128.3, 128.6, 131.5, 136.0, 155.8, 162.5 (NHC(CH₃)₂C₁₀H₆). IR (cm^{−1}, KBr): 3335 (m), 3223 (m), 3143 (w), 3024 (w), 2974 (w), 2909 (w), 1575 (m), 1032 (m), 810 (m), 739 (m). Anal. Calcd for C₂₂H₂₆NiIr: C 53.20, H 5.28, N 2.82. Found: C 52.75, H 5.36, N 2.87.

General Procedure for Synthesis of Cp*IrH[κ²(N,C)-(NH₂CR₂-2-C₆H₄)] (3a: R = C₆H₅, 3b: R = CH₃). Cp*Ir[κ²(N,C)-(NHCR₂-2-C₆H₄)] (2) (0.69 mmol) in 2-propanol (10 mL) was stirred at room temperature overnight. The solvent was removed under reduced pressure. The residue was washed with hexane and dried under vacuum.

Cp*IrH[κ²(N,C)-(NH₂C(C₆H₅)₂-2-C₆H₄)] (3a). Isolated yield: 88% (0.23 g, 0.39 mmol). ¹H NMR (300.4 MHz, CD₂Cl₂, rt, δ/ppm): −12.92 (s, 1H; IrH), 1.84 (s, 15H; C(CH₃)₅), 4.33, 5.78 (each br, 1H; NH₂C(C₆H₅)₂C₆H₄), 6.63–7.45 (m, 14H; NH₂C(C₆H₅)₂C₆H₄). ¹³C{¹H} NMR (75.6 MHz, CD₂Cl₂, rt, δ/ppm): 9.9 (C₅(CH₃)₅), 80.3 (NH₂C(C₆H₅)₂C₆H₄), 87.4 (C₅(CH₃)₅), 120.0, 126.0, 126.2, 127.5, 128.3, 128.4, 128.6, 128.7, 129.1, 137.3, 146.5, 148.0, 152.9, 153.5 (NH₂C(C₆H₅)₂C₆H₄). IR (cm^{−1}, KBr): 3363 (w), 3351 (w), 3298 (m), 3049 (m), 3019 (m), 2966 (m), 2902 (m), 2851 (m), 2024 (s), 1570 (s), 1261 (s), 1025 (m), 702 (m). Anal. Calcd for C₂₉H₃₂NiIr: C 59.36, H 5.50, N 2.39. Found: C 59.33, H 5.59, N 2.20.

Cp*IrH[κ²(N,C)-(NH₂C(CH₃)₂-2-C₆H₄)] (3b). Isolated yield: 86% (0.27 g, 0.59 mmol). ¹H NMR (300.4 MHz, CD₂Cl₂, rt, δ/ppm): −13.23 (s, 1H; IrH), 1.27, 1.48 (each s, 3H; NH₂C(CH₃)₂C₆H₄), 1.93 (s, 15H; C(CH₃)₅), 3.21, 4.47 (each br, 1H; NH₂C(CH₃)₂C₆H₄), 6.62 (d, ³J_{HH} = 7.3 Hz, 1H; NH₂C(CH₃)₂C₆H₄), 6.72 (t, ³J_{HH} = 7.3 Hz, 1H; NH₂C(CH₃)₂C₆H₄), 6.79 (t, ³J_{HH} = 7.3 Hz, 1H; NH₂C(CH₃)₂C₆H₄), 7.32 (d, ³J_{HH} = 7.3 Hz, 1H; NH₂C(CH₃)₂C₆H₄). ¹³C{¹H} NMR (75.6 MHz, CD₂Cl₂, rt, δ/ppm): 9.4 (C₅(CH₃)₅), 28.8, 30.9 (NH₂C(CH₃)₂C₆H₄), 66.9 (NH₂C(CH₃)₂C₆H₄), 87.2 (C₅(CH₃)₅), 117.4, 118.2, 120.3, 120.6, 126.1, 137.3 (NH₂C(CH₃)₂C₆H₄). IR (cm^{−1}, KBr): 3306 (m), 3262 (m), 3042 (m), 2968 (m), 2912 (m), 2064 (s), 1583 (m), 1571 (m), 1403 (m), 744 (m). Anal. Calcd for C₁₉H₂₈NiIr: C 49.33, H 6.10, N 3.03. Found: C 49.11, H 6.13, N 3.04.

Synthesis of Cp*IrD[κ²(N,C)-(NH₂C(CH₃)₂-2-C₆H₄)] (3b-D). C₂H₅CD(OH)C₂H₅ (0.031 mL, 0.28 mmol) was added to a solution of Cp*Ir[κ²(N,C)-(NHC(CH₃)₂-2-C₆H₄)] (2b) (0.13 g, 0.28 mmol). The solution color turned from purple to yellow. The reaction mixture was stirred at room temperature for 4 weeks. Then, the solvent was removed under reduced pressure. Deuteride complex **3b-D** was obtained in 87% yield (0.11 g, 0.24 mmol). ¹H NMR (300.4 MHz, THF-*d*₈, rt, δ/ppm): 1.12, 1.64 (each s, 3H; NH₂C(CH₃)₂C₆H₄), 1.70 (s, 15H; C(CH₃)₅), 4.38, 4.92 (each br, 1H; NH₂C(CH₃)₂C₆H₄), 6.67 (d, ³J_{HH} = 4.6 Hz, 1H; NH₂C(CH₃)₂C₆H₄), 6.75–6.81 (m, 2H; NH₂C(CH₃)₂C₆H₄), 7.35 (d, ³J_{HH} = 7.3 Hz, 1H; NH₂C(CH₃)₂C₆H₄). ²H NMR (46.1 MHz, THF, rt, δ/ppm): −13.34 (s, 1H; Ir-D).

Synthesis of Cp*Ir(OCOCH₃)[κ²(N,C)-(NH₂C(C₆H₅)₂-2-C₆H₄)] (4). Method A: Acetic acid (0.010 mL, 0.14 mmol) was added to a solution of Cp*Ir[κ²(N,C)-(NHC(C₆H₅)₂-2-C₆H₄)] (2a) (0.084 g, 0.14 mmol) in CH₂Cl₂ (5 mL). The solution color turned from purple to yellow. The reaction mixture was stirred at room temperature for 21 h. After the solvent was removed under reduced pressure, the residue was recrystallized from toluene and hexane. Isolated yield: 53% (0.11 g, 0.074 mmol). Method B: A mixture of Cp*Ir(OCOCH₃)₂ (0.15 g, 0.30 mmol) and triphenylmethylamine (0.078 g, 0.30 mmol) in CH₂Cl₂ (6 mL) was stirred at room temperature for 20 h. The solvent was removed under reduced pressure. Recrystallization from toluene and hexane afforded yellow crystals. Isolated yield: 36% (0.076 g, 0.11 mmol). ¹H NMR (300.4 MHz, CD₂Cl₂, rt, δ/ppm): 1.36 (s, 15H; C(CH₃)₅), 1.91 (s, 3H; OCOCH₃), 4.85, 8.51 (each br, 1H; NH₂C(C₆H₅)₂C₆H₄), 6.26–7.77 (m, 14H; NH₂C(C₆H₅)₂C₆H₄). ¹³C{¹H} NMR (75.6 MHz, CD₂Cl₂, rt, δ/ppm): 8.98 (C₅(CH₃)₅), 25.7 (OCOCH₃), 79.9 (NH₂C(C₆H₅)₂C₆H₄), 85.9 (C₅(CH₃)₅), 122.4, 126.6, 127.1, 127.2, 127.4, 128.3, 128.4, 128.7, 129.0, 129.2, 136.0, 146.6, 155.2, 159.0 (NH₂C(C₆H₅)₂C₆H₄), 180.6 (OCOCH₃). IR (cm^{−1}, KBr): 3304(w), 3233 (w), 3051(w), 2982(w), 2909(w), 1604 (s), 1574(m),

1445(m), 1367(m), 1314(m), 1035(w), 762(m), 752(m), 732(m), 701(m). Anal. Calcd for C₃₁H₃₄NO₂Ir: C 57.74, H 5.31, N 2.17, O 4.96. Found: C 57.67, H 5.60, N 2.11, O 5.32.

Synthesis of Cp*Ir[CH(COOCH₃)₂][κ²(N,C)-(NH₂C(C₆H₅)₂-2-C₆H₄)] (5). Dimethyl malonate (0.031 mL, 0.27 mmol) was added to a solution of Cp*Ir[κ²(N,C)-(NHC(C₆H₅)₂-2-C₆H₄)] (2a) (0.158 g, 0.27 mmol) in CH₂Cl₂ (10 mL). The solution color turned from purple to yellow. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure. The residue was washed with hexane and then dried *in vacuo*. Isolated yield: 84% (0.16 g, 0.23 mmol). ¹H NMR (300.4 MHz, CD₂Cl₂, rt, δ/ppm): 1.30 (s, 15H; C(CH₃)₅), 2.80, 3.60 (each s, 3H; COOCH₃), 4.09 (s, 1H; IrCH), 4.33, 7.19 (each br, 1H; NH₂C(C₆H₅)₂C₆H₄), 6.30–7.52 (m, 14H; NH₂C(C₆H₅)₂C₆H₄). ¹³C{¹H} NMR (75.6 MHz, CD₂Cl₂, rt, δ/ppm): 8.5 (C₅(CH₃)₅), 49.8, 50.6 (COOCH₃), 59.8 (IrCH), 80.5 (NH₂C(C₆H₅)₂C₆H₄), 88.4 (C₅(CH₃)₅), 121.4, 125.9, 127.2, 128.1, 128.4, 128.5, 128.7, 129.6, 129.7, 137.0, 147.6, 148.1, 152.3, 155.6 (NH₂C(C₆H₅)₂C₆H₄), 175.3, 177.7 (COOCH₃). IR (cm^{−1}, KBr): 3299 (w), 3277 (w), 3056 (w), 2944 (w), 1674 (s), 1575 (m), 1443 (m), 1432 (m), 1263 (m), 1136 (m), 1059 (m), 703 (m). Anal. Calcd for C₃₄H₃₈NO₄Ir: C 56.96, H 5.34, N 1.95. Found: C 57.24, H 5.56, N 1.90.

General Procedure for the Synthesis of Cp*Ir(CH₂COCH₃)[κ²(N,C)-(NH₂CR₂-2-C₆H₄)] (6a: R = C₆H₅, 6b: R = CH₃). A solution of Cp*Ir[κ²(N,C)-(NHCR₂-2-C₆H₄)] (2) (0.154 mmol) in acetone (15 mL) was stirred at room temperature overnight. After the solvent was removed under reduced pressure, the residue was washed with hexane. Recrystallization from acetone afforded orange crystals.

Cp*Ir(CH₂COCH₃)[κ²(N,C)-(NH₂C(C₆H₅)₂-2-C₆H₄)] (6a). Isolated yield: 87% (0.086 g, 0.13 mmol). ¹H NMR (300.4 MHz, CD₂Cl₂, rt, δ/ppm): 1.36 (s, 15H; C(CH₃)₅), 1.99 (s, 3H; IrCH₂COCH₃), 2.27, 3.00 (each d, ²J_{HH} = 5.9 Hz, 1H; IrCH₂COCH₃), 4.40, 6.80 (each br, 1H; NH₂C(C₆H₅)₂C₆H₄), 6.18–7.35 (m, 14H; NH₂C(C₆H₅)₂C₆H₄). ¹³C{¹H} NMR (75.6 MHz, CD₂Cl₂, rt, δ/ppm): 8.8 (C₅(CH₃)₅), 17.8 (CH₂COCH₃), 29.5 (CH₂COCH₃), 81.1 (NH₂C(C₆H₅)₂C₆H₄), 87.2 (C₅(CH₃)₅), 121.0, 126.8, 127.1, 127.3, 128.1, 128.3, 128.6, 129.6, 129.8, 136.2, 146.8, 148.5, 152.5, 157.3 (NH₂C(C₆H₅)₂C₆H₄), 213.8 (CO). IR (cm^{−1}, KBr): 3325 (w), 3144 (w), 3056 (w), 2971 (w), 2910 (w), 1596 (s), 1574 (s), 1443 (m), 1250 (s), 1047 (m). Anal. Calcd for C₃₂H₃₆NOIr: C 59.79, H 5.64, N 2.18. Found: C 59.61, H 5.91, N 1.86.

Cp*Ir(CH₂COCH₃)[κ²(N,C)-(NH₂C(CH₃)₂-2-C₆H₄)] (6b). Isolated yield: 81% (0.063 g, 0.12 mmol). ¹H NMR (300.4 MHz, CD₂Cl₂, rt, δ/ppm): 1.27, 1.46 (each s, 3H; NH₂C(CH₃)₂C₆H₄), 1.65 (s, 3H; IrCH₂COCH₃), 1.70 (s, 15H; C(CH₃)₅), 2.55 (AB pattern, ²J_{HH} = 9.1 Hz, 2H; IrCH₂COCH₃), 3.12, 5.57 (each br, 1H; NH₂C(CH₃)₂C₆H₄), 6.63–6.72 (m, 2H; NH₂C(CH₃)₂C₆H₄), 6.79–6.85 (m, 1H; NH₂C(CH₃)₂C₆H₄), 7.18–7.21 (m, 1H; NH₂C(CH₃)₂C₆H₄). ¹³C{¹H} NMR (75.6 MHz, CD₂Cl₂, rt, δ/ppm): 9.1 (C₅(CH₃)₅), 15.3 (CH₂COCH₃), 30.7 (CH₂COCH₃), 30.2, 32.4 (NH₂C(CH₃)₂-C₆H₄), 66.6 (NH₂C(CH₃)₂C₆H₄), 86.8 (C₅(CH₃)₅), 121.1, 121.3, 126.6, 136.6, 152.7, 155.1 (NH₂C(CH₃)₂C₆H₄), 216.9 (CO). IR (cm^{−1}, KBr): 3309 (w), 3140 (w), 3107 (w), 3042 (w), 2963 (m), 2905 (m), 1553 (s), 1260 (m), 1094 (m), 1024 (m), 798 (m), 726 (m). Anal. Calcd for C₂₂H₃₂NOIr: C 50.94, H 6.22, N 2.70. Found: C 50.58, H 6.36, N 2.40.

General Procedure for Synthesis of Carbonyl Complexes [Cp*Ir(CO)[κ²(N,C)-(NH₂CR₂-2-C₆H₄)](BF₄) (7a: R = C₆H₅, 7b: R = CH₃) and [Cp*Ir[κ²(N,N')-(S,S)-Tscydnl(CO)](BF₄) (8). To an acetonitrile solution (8 mL) of the chloride complex Cp*IrCl[κ²(N,C)-(NH₂CR₂-2-C₆H₄)] (1) or Cp*IrCl[κ²(N,N')-(S,S)-Tscydnl]²⁺ (0.15 mmol) was added AgBF₄ (0.15 mmol). Then, the reaction mixture was stirred at room temperature for 21 h. After filtration through a Celite pad, the solvent was removed under reduced pressure. The residue was redissolved in CH₂Cl₂. After bubbling of CO gas (0.1 MPa) into the reaction mixture for 30 min, the

Table 1. Crystallographic Data for 2a, 4, 6b, and 7b

	2a	4	6b	7b
empirical formula	C ₂₉ H ₃₀ IrN	C ₃₁ H ₃₄ IrNO ₂	C ₂₂ H ₃₂ IrN	C ₂₀ H ₂₇ BF ₄ IrNO
fw	584.78	644.84	518.72	576.46
cryst color	purple	orange	yellow	colorless
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$ (#2)	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>P</i> $\bar{1}$ (#2)	<i>P</i> 2 ₁ / <i>c</i> (#14)
<i>a</i> , Å	7.870(3)	10.922(4)	9.092(4)	8.626(3)
<i>b</i> , Å	10.155(4)	19.511(7)	9.101(5)	15.356(5)
<i>c</i> , Å	15.749(7)	12.677(5)	25.409(11)	16.209(5)
α , deg	73.934(12)		90.061(8)	
β , deg	84.275(12)	95.293(5)	90.049(4)	91.429(4)
γ , deg	74.846(15)		104.137(10)	
<i>V</i> , Å ³	1166.9(8)	2689.8(17)	2038.7(17)	2146.3(12)
<i>Z</i>	2	4	4	4
<i>D</i> _{calcd} , g cm ⁻³	1.664	1.592	1.690	1.784
<i>F</i> ₀₀₀	576.00	1280.00	1024.00	1120.00
μ , cm ⁻¹ (Mo K α)	57.528	50.048	65.763	62.813
exposure rate, sec ^o	6.0	2.0	2.0	10.0
no. of reflections measured	8570	20929	15937	16276
no. of unique reflections	4916	6118	8888	4845
no. variables	310	398	521	286
<i>R</i> ₁ [<i>I</i> > 2.00 σ (<i>I</i>)] ^a	0.0249	0.0377	0.0373	0.0431
<i>wR</i> ₂ (all reflections) ^a	0.0654	0.0913	0.1014	0.1122
GOF on <i>F</i> ²	0.999	1.000	1.001	1.001

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|, wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}.$$

solvent was evaporated under vacuum. Recrystallization from CH₂Cl₂ and hexane afforded colorless crystals.

[Cp*Ir{ κ^2 (*N,C*)-(NH₂C(C₆H₅)₂-2-C₆H₄)}(CO)]BF₄ (7a). Isolated yield: 62% (0.067 g, 0.090 mmol). ¹H NMR (300.4 MHz, CD₂Cl₂, rt, δ /ppm): 1.78 (s, 15H; C(CH₃)₅), 5.15, 6.65 (each br, 1H; NH₂C(C₆H₅)₂C₆H₄), 6.40–7.45 (m, 14H; NH₂C(C₆H₅)₂C₆H₄). ¹³C{¹H} NMR (75.6 MHz, CD₂Cl₂, rt, δ /ppm): 8.7 (C₅(CH₃)₅), 81.3 (C₅(CH₃)₅), 100.7 (NH₂C(C₆H₅)₂C₆H₄), 127.8, 128.1, 128.46, 128.54, 128.65, 128.75, 129.0, 129.2, 134.9, 136.7, 143.4, 144.45, 144.47, 154.8 (NH₂C(C₆H₅)₂C₆H₄), 168.3 (IrCO). IR (cm⁻¹, KBr): 3057 (w), 2963 (w), 2030 (s), 1576 (m), 1261 (m), 1088 (m), 1022 (m), 801 (m). The isolated complex was not stable enough to be subjected to elemental analysis.

[Cp*Ir{ κ^2 (*N,C*)-(NH₂C(CH₃)₂-2-C₆H₄)}(CO)]BF₄ (7b). Isolated yield: 67% (0.064 g, 0.10 mmol). ¹H NMR (300.4 MHz, CD₂Cl₂, rt, δ /ppm): 1.50, 1.61 (each s, 3H; NH₂C(CH₃)₂C₆H₄), 2.01 (s, 15H; C(CH₃)₅), 4.46, 5.38 (each br, 1H; NH₂C(CH₃)₂C₆H₄), 6.85 (d, ³*J*_{HH} = 7.1 Hz, 1H; NH₂C(CH₃)₂C₆H₄), 7.05–7.15 (m, 2H; NH₂C(CH₃)₂C₆H₄), 7.23 (d, ³*J*_{HH} = 7.1 Hz, 1H; NH₂C(CH₃)₂C₆H₄). ¹³C{¹H} NMR (75.6 MHz, CD₂Cl₂, rt, δ /ppm): 9.1 (C₅(CH₃)₅), 29.3, 30.8 (NH₂C(CH₃)₂C₆H₄), 68.9 (C₅(CH₃)₅), 100.8 (NH₂C-(CH₃)₂C₆H₄), 123.4, 126.0, 128.2, 131.9, 136.3, 157.2 (NH₂C(CH₃)₂C₆H₄), 168.7 (IrCO). IR (cm⁻¹, KBr): 3289 (m), 3262 (m), 3178 (w), 2983 (m), 2036 (s), 1456 (w), 1084 (m), 1029 (m). The isolated complex was not stable enough to be subjected to elemental analysis.

[Cp*Ir{ κ^2 (*N,N'*)-(S,S)-Tscydn}(CO)]BF₄ (8). Isolated yield: 57% (0.053 g, 0.075 mmol). ¹H NMR (300.4 MHz, CD₂Cl₂, rt, δ /ppm): 1.97 (s, 15H; C(CH₃)₅), 2.23 (s, 3H; SO₂C₆H₄CH₃), 0.512.72 (m, 10H, N(C₆H₁₀)NH₂), 4.63, 4.93 (each br, 2H, N(C₆H₁₀)NH₂), 7.29, 7.69 (each d, *J* = 7.8 Hz, *J* = 8.1 Hz SO₂C₆H₄CH₃). ¹³C{¹H} NMR (75.6 MHz, CD₂Cl₂, rt, δ /ppm): 9.4 (C₅(CH₃)₅), 21.6, 24.7, 25.0, 34.6, 34.8, 67.4, 69.4 ((C₆H₁₀)NH₂, SO₂C₆H₄CH₃), 101.8 (C₅(CH₃)₅), 127.9, 129.9, 138.6, 143.3, 167.7 (SO₂C₆H₄CH₃), 194.0 (IrCO). IR (cm⁻¹, KBr): 3296 (m), 3263 (m), 3176 (w), 2960 (m),

2926 (m), 2863 (m), 2056 (s), 1262 (m), 1031 (m), 888(w). The isolated complex was not stable enough to be subjected to elemental analysis.

X-ray Structure Determinations of 2a, 4, 6b, and 7b. All measurements were made on a Rigaku Saturn CCD area detector equipped with graphite-monochromated Mo K α radiation (λ = 0.71070 Å) under a nitrogen stream at 193 K. Indexing was performed from seven images. The crystal-to-detector distance was 45.05 mm. The data were collected to a maximum 2θ value of 55.0°. A total of 720 oscillation images were collected. A sweep of data was carried out using ω scans from -110.0° to 70.0° in 0.5° steps, at χ = 45.0° and φ = 0.0°. A second sweep was performed using ω scans from -110.0° to 70.0° in 0.5° steps, at χ = 45.0° and φ = 90.0°. Intensity data were corrected for Lorentz–polarization effects as well as absorption. Structure solution and refinements were performed with the Crystal Structure program package. The heavy atom positions were determined by a direct program method (SIR2002), and the remaining non-hydrogen atoms were found by subsequent Fourier techniques (DIRDIF99). An empirical absorption correction based on equivalent reflections was applied to all data. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques based on *F*². All hydrogen atoms were constrained to ride on their parent atom. Relevant crystallographic data are compiled in Table 1.

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Supporting Information Available: X-ray crystallographic data of **1a**, **1b**, **2a**, **2b**, **4**, **6b**, and **7b** and experimental details for determination of thermodynamic parameters in the reaction of **2a** and acetone are available free of charge via the Internet at <http://pubs.acs.org>.

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