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

Sachiko Arita, Takashi Koike, Yoshihito Kayaki, and Takao Ikariya*

Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, O-okayama 2-12-1, Meguro-ku, Tokyo 152-8552, Japan

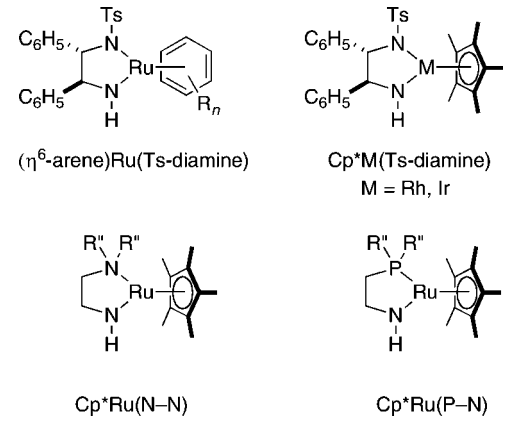
Received February 13, 2008

A series of 16-electron Cp*Ir amide complexes with C−N chelating ligands, Cp*Ir[κ^2(*N*,*C*)-(NHCR$_2$-2-C$_6$H$_4$)] (**2a**: R = C$_6$H$_5$, **2b**: R = CH$_3$), and the chiral version, Cp*Ir[κ^2(*N*,*C*)-(*R*)-{NHCH(CH$_3$)-2-C$_{10}$H$_6$}] (**2e**), were obtained in good to excellent yields from reactions of 18-electron iridium amine complexes, Cp*IrCl[κ^2(*N*,*C*)-(NH$_2$CR$_2$-2-C$_6$H$_4$)] (**1a**: R = C$_6$H$_5$, **1b**: R = CH$_3$) and Cp*IrCl[κ^2(*N*,*C*)-(*R*)-{NH$_2$CH(CH$_3$)-2-C$_{10}$H$_6$}] (**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[κ^2(*N*,*N*′)-TsNCHC$_6$H$_5$CHC$_6$H$_5$NH](η^6-arene) and Cp*M[κ^2(*N*,*N*′)-TsNCHC$_6$H$_5$CHC$_6$H$_5$NH] (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 the ligand from *N*-sulfonylated diamines (Ts-diamine) to the *N*,*N*-dimethylaminoethylamines (N−N) and 2-phosphinoethylamines (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 H$_2$ under mild conditions, both Cp*Ru(N−N) and Cp*Ru(P−N) complexes readily activate H$_2$ with help from protic solvents[4a,b,d,5] and can efficiently catalyze

Chart 1



* Corresponding author. Tel: +81-3-5734-2636. Fax: +81-3-5734-2637. E-mail: tikariya@apc.titech.ac.jp.

(1) Recent review articles for metal-based bifunctional catalysts: (a) Ikariya, T.; Murata, K.; Noyori, R. *Org. Biomol. Chem.* **2006**, *4*, 393–406. (b) Muñiz, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 6622–6627. (c) Shibasaki, M.; Matsunaga, S. *Chem. Soc. Rev.* **2006**, *35*, 269–279. (d) Ma, J.-A.; Cahard, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 4566–4583. (e) Gröger, H. *Chem.−Eur. J.* **2001**, *7*, 5246–5251.

(2) (a) Ikariya, T.; Blacker, A. J. *Acc. Chem. Res.* **2007**, *40*, 1300–1308. (b) Hashiguchi, S.; Fujii, A.; Takehara, J.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 7562–7563. (c) Fujii, A.; Hashiguchi, S.; Uematsu, N.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 2521–2522. (d) Uematsu, N.; Fujii, A.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 4916–4917. (e) Haack, K.-J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 285–288. (f) Hashiguchi, S.; Fujii, A.; Haack, K.-J.; Matsumura, K.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 288–290. (g) Murata, K.; Ikariya, T.; Noyori, R. J. *Org. Chem.* **1999**, *64*, 2186–2187. (h) Murata, K.; Okano, K.; Miyagi, M.; Iwane, H.; Noyori, R.; Ikariya, T. *Org. Lett.* **1999**, *1*, 1119–1121. (i) Koike, T.; Murata, K.; Ikariya, T. *Org. Lett.* **2000**, *2*, 3833–3836. (j) Okano, K.; Murata, K.; Ikariya, T. *Tetrahedron Lett.* **2000**, *41*, 9277–9280. (k) Watanabe, M.; Murata, K.; Ikariya, T. *J. Org. Chem.* **2002**, *67*, 1712–1715. (l) Hamada, T.; Torii, T.; Izawa, K.; Noyori, R.; Ikariya, T. *Org. Lett.* **2002**, *4*, 4373–4376. (m) Hamada, T.; Torii, T.; Izawa, K.; Ikariya, T. *Tetrahedron* **2004**, *60*, 7411–7417.

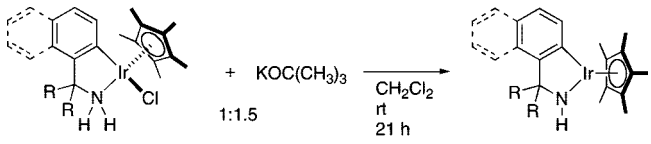
(3) (a) Murata, K.; Konishi, H.; Ito, M.; Ikariya, T. *Organometallics* **2002**, *21*, 253–255. (b) Watanabe, M.; Murata, K.; Ikariya, T. *J. Am. Chem. Soc.* **2003**, *125*, 7508–7509. (c) Ikariya, T.; Wang, H.; Watanabe, M.; Murata, K. *J. Organomet. Chem.* **2004**, *689*, 1377–1381. (d) Watanabe, M.; Ikagawa, A.; Wang, H.; Murata, K.; Ikariya, T. *J. Am. Chem. Soc.* **2004**, *126*, 11148–11149. (e) Wang, H.; Watanabe, M.; Ikariya, T. *Tetrahedron Lett.* **2005**, *46*, 963–966. (f) Hasegawa, Y.; Watanabe, M.; Gridnev, I. D.; Ikariya, T. *J. Am. Chem. Soc.* **2008**, *130*, 2158−2159.

(4) (a) Ito, M.; Hirakawa, M.; Murata, K.; Ikariya, T. *Organometallics* **2001**, *20*, 379–381. (b) Ito, M.; Hirakawa, M.; Osaku, A.; Ikariya, T. *Organometallics* **2003**, *22*, 4190–4192. (c) Ito, M.; Kitahara, S.; Ikariya, T. *J. Am. Chem. Soc.* **2005**, *127*, 6172–6173. (d) Ito, M.; Sakaguchi, A.; Kobayashi, C.; Ikariya, T. *J. Am. Chem. Soc.* **2007**, *129*, 290–291. (e) Ito, M.; Osaku, A.; Shiibashi, A.; Ikariya, T. *Org. Lett.* **2007**, *9*, 1821–1824.

(5) Hedberg, C.; Källstöm, K.; Arvidsson, P. I.; Brandt, P.; Andersson, P. G. *J. Am. Chem. Soc.* **2005**, *127*, 15083–15090.

10.1021/om800124f CCC: $40.75
Publication on Web 05/15/2008

Scheme 1



1a: R = C_6H_5 **2a**: 80% yield
1b: R = CH_3 **b**: 88%
1e: (*R*)-1-(1-naphthyl)ethylamine **e**: 63%

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[κ^2(*N*,*C*)-(NHCR$_2$-2-C_6H_4)], and their chiral version, Cp*Ir[κ^2(*N*,*C*)-(*R*)-{NHCH(CH_3)-2-$C_{10}H_6$}].

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[κ^2-(*N*,*C*)-(NHCR$_2$-2-C_6H_4)] (**2a**: R = C_6H_5, **2b**: R = CH_3) and Cp*Ir[κ^2(*N*,*C*)-(*R*)-{NHCH(CH_3)-2-$C_{10}H_6$}] (**2e**) were obtained as purple solids in good yields from the reaction of the Ir chloride complexes Cp*IrCl[κ^2(*N*,*C*)-(NH$_2$CR$_2$-2-C_6H_4)] (**1a**: R = C_6H_5, **1b**: R = CH_3) and Cp*IrCl[κ^2(*N*,*C*)-(*R*)-{NHCH(CH_3)-2-$C_{10}H_6$}] (**1e**) with 1.5 equiv of KOC(CH_3)$_3$ in CH_2Cl_2 at room temperature (Scheme 1). Single-crystal X-ray crystallgraphy 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−NH$_2$ bond, 2.137 Å, in the chloro complex **1a** (see the Supporting Information), as observed in analogous amido− and (hydrido)amine−Ru complexes.[2e] The ^{1}H NMR spectrum of **2a** in CD_2Cl_2 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 NH$_2$ signals of the parent complex **1a** (4.97 and 5.72 ppm), possibly due to the sp^2 hybridization at the nitrogen atom. Similarly, ^{1}H NMR spectroscopic data in the amido complexes **2b** and **2e** display the NH signal at 8.47 and 8.42 ppm, respectively.

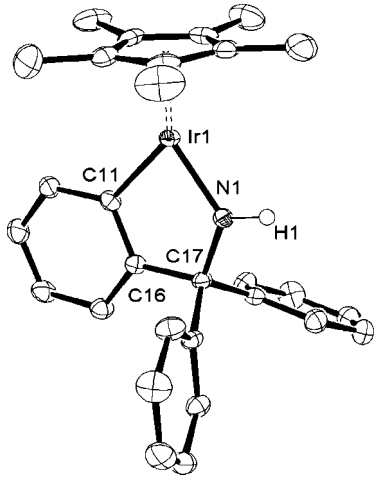


Figure 1. Molecular structure of Cp*Ir[κ^2(*N*,*C*)-{NHC(C_6H_5)$_2$-2-C_6H_4}] (**2a**). The hydrogen atoms are omitted for clarity, and the ellipsoids represent 50% probability.

The starting neutral chloride complexes **1a** and **1b** were readily prepared from the reaction of [Cp*IrCl$_2$]$_2$ and primary benzylamines ($C_6H_5CR_2NH_2$; R = C_6H_5 and CH_3) in the presence of $NaOCOCH_3$ in CH_2Cl_2 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 cycloiridation was found to proceed through formation of the monomeric κ^1(*N*)-amine complex Cp*IrCl$_2$[κ^1(*N*)-NH$_2$CR$_2$C$_6$H$_5$] to give complexes **1a** and **1b**. Notably, the cyclometalation step[8] 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 Davies[9] and us.[10] In fact, an isolable bis(acetato)−Ir complex, Cp*Ir(OCOCH$_3$)$_2$, readily reacted with triphenylmethylamine 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, CH_3), **1d** (R = H, H), **1e**, and **1f** (R = H, $CH_2OSi(CH_3)_2{}^tBu$), bearing sterically less hindered amines with good yields and selectivities, although the reaction required a higher reaction temperature of 60 °C in CH_3CN. These results imply that the substituents on the α-carbon bound to the NH$_2$ 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[κ^2-(*N*,*C*)-{NH$_2$C(C_6H_5)$_2$-2-C_6H_4}] (**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 ^{1}H NMR spectra of **3a** and **3b** in CD_2Cl_2 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**.

(6) (a) Sortais, J.-B.; Ritleng, V.; Voelklin, A.; Holuigue, A.; Smail, H.; Barloy, L.; Sirlin, C.; Verzijl, G. K. M.; Boogers, J. A. F.; de Vries, A. H. M.; de Vries, J. G.; Pfeffer, M. *Org. Lett.* **2005**, *7*, 1247–1250. (b) Sortais, J.-B.; Pannetier, N.; Holuigue, A.; Barloy, L.; Sirlin, C.; Pfeffer, M.; Kyritsakas, N. *Organometallics* **2007**, *26*, 1856–1867. (c) Sortais, J.-B.; Pannetier, N.; Clément, N.; Barloy, L.; Sirlin, C.; Pfeffer, M.; Kyritsakas, N. *Organometallics* **2007**, *26*, 1868–1874.

(7) Barloy and Pfeffer have reported that an analogous iridacycle was not obtained as a single product by the reaction of the primary amine in the presence of KPF_6: see ref 6b.

(8) For reviews of cyclometalation, see for example: (a) Dehand, M.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327–352. (b) Omae, I. *Coord. Chem. Rev.* **1988**, *83*, 137–167. (c) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403–424. (d) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759–1792.

(9) (a) Davies, D. L.; Al-Duaij, O.; Fawcett, J.; Giardiello, M.; Hilton, S. T.; Russell, D. R. *Dalton Trans.* **2003**, 4132−4138. (b) Davies, D. L.; Donald, S. M. A.; Al-Duaij, O.; Macgregor, S. A.; Pölleth, M. *J. Am. Chem. Soc.* **2006**, *128*, 4210–4211.

(10) (a) Koike, T.; Ikariya, T. *Organometallics* **2005**, *24*, 724–730. (b) Ishiwata, K.; Kuwata, S.; Ikariya, T. *Organometallics* **2006**, *25*, 5847–5849.

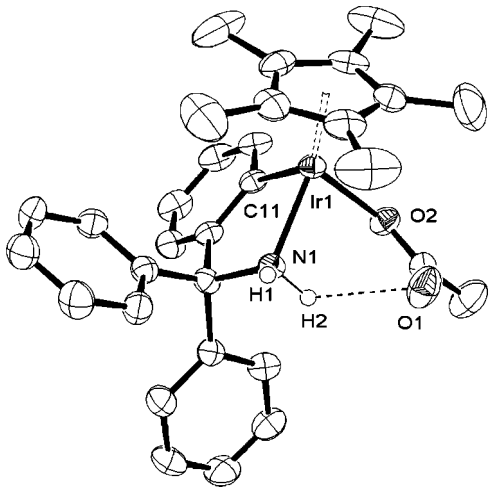
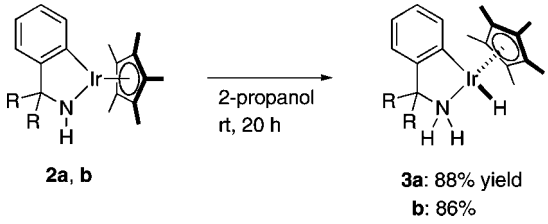


Figure 2. Molecular structure of $Cp^*Ir(OCOCH_3)[\kappa^2(N,C)$-$\{NH_2C(C_6H_5)_2$-2-$C_6H_4\}]$ (**4**). Ellipsoids are shown at the 50% probability level for the non-hydrogen atoms. The dashed line indicates the hydrogen bond.

Scheme 2

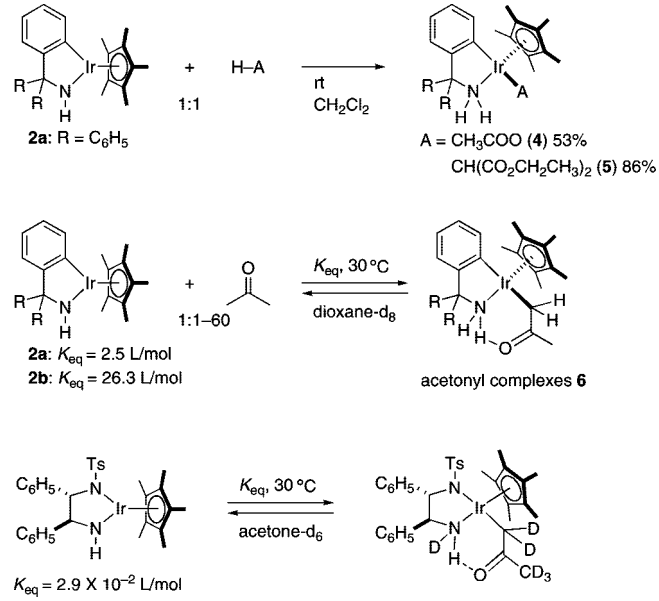


These hydrido complexes were found to be thermally stable under an Ar atmosphere. Thermal treatment of the 18-electron deuterido(amine) complex **3b-D** in 1,4-dioxane at 100 °C provided no deuterido scrambling on this complex, indicating that neither reductive elimination of the hydrido ligand and phenyl fragment on the C−N chelate ligand followed by recyclometalation of the $\kappa^1(N)$-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 (pK_a in DMSO = 12.3)[15] in CH_2Cl_2 at room temperature gave the corresponding acetato complex **4**, $Cp^*Ir(OCOCH_3)[\kappa^2(N,C)$-$\{NH_2C(C_6H_5)_2$-2-$C_6H_4\}]$, which was also obtained from the cyclometalation of $Cp^*Ir(OCOCH_3)_2$ 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 $N(H_2)\cdots O{=}C$ distance of 2.945(3) Å, indicating the presence of an intramolecular hydrogen bond, as observed in the analogous complexes.[14,16] The $N(H)\cdots O{=}C$ 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 (pK_a in DMSO = 15.9)[15] to give the corresponding C-bound malonato complex **5**, $Cp^*Ir[CH(COOCH_3)_2][\kappa^2(N,C)$-$\{NH_2C(C_6H_5)_2$-2-$C_6H_4\}]$, in 86% yield, as observed in the isolable Ru complex.[3b] The $^{13}C\{^1H\}$ NMR of **5** in CD_2Cl_2 displayed characteristic C=O signals of $CH(COOCH_3)_2$ at 175.3 and 177.7 ppm. The deprotonation by the amido−Ir complex **2** was also observed for less acidic acetone (pK_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**, $Cp^*Ir(CH_2COCH_3)[\kappa^2(N,C)$-$\{NH_2C(C_6H_5)_2$-2-$C_6H_4\}]$, 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 $^2J_{HH}$ = 5.9 Hz and two distinct signals due to NH protons at 4.40 and 6.80 ppm. Because the presence of the C=O moiety was confirmed by a $^{13}C\{^1H\}$ 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 $Cp^*Ir(CH_2COCH_3)$(Tsdpen) (dpen = 1,2-diphenylethylenediamine) complex. Similar spectroscopic features were observed for the related acetonyl(amine)

(11) (a) Arita, S.; Koike, T.; Kayaki, Y.; Ikariya, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 2447–2449. (b) Recently, dehydrogenation of hydrido(amine) complex to amido complex by molecular oxygen was also reported in a related Ts-diamine system: Heiden, Z. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2007**, *129*, 14303–14310.

(12) Ohkuma, T.; Ooka, H.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 2675–2676.

(13) (a) Abdur-Rashid, K.; Clapham, S. E.; Hadzovic, A.; Harvey, J. N.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 15104–15118. (b) Alonso, D. A.; Brandt, P.; Nordin, S. J. M.; Andersson, P. G. *J. Am. Chem. Soc.* **1999**, *121*, 9580–9588. (c) Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 1466–1478.

(14) Koike, T.; Ikariya, T. *Adv. Synth. Catal.* **2004**, *346*, 37–41.

(15) (a) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463. (b) Arnett, E. M.; Maroldo, S. G.; Schilling, S. L.; Harrelson, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6759–6767.

(16) Koike, T.; Ikariya, T. *J. Organomet. Chem.* **2007**, *692*, 408–419.

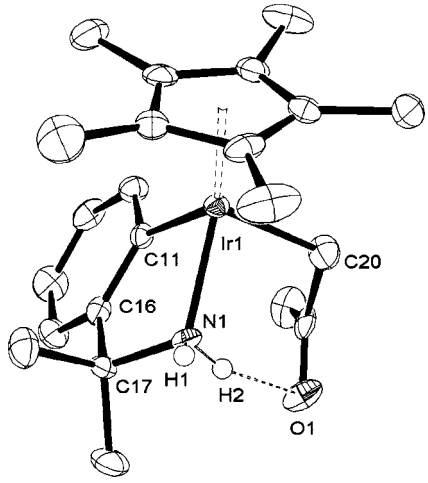


Figure 3. Molecular structure of $Cp^*Ir(CH_2COCH_3)[\kappa^2(N,C)$-$\{NH_2C(CH_3)_2$-2-$C_6H_4\}]$ (**6b**). Only one of the two independent molecules is shown. Ellipsoids are shown at the 50% probability level for the non-hydrogen atoms. The dashed line indicates the hydrogen bond.

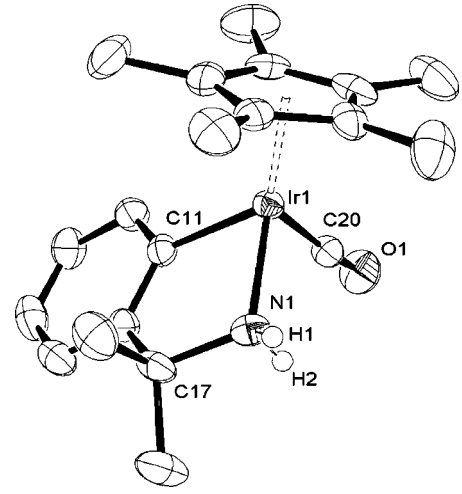


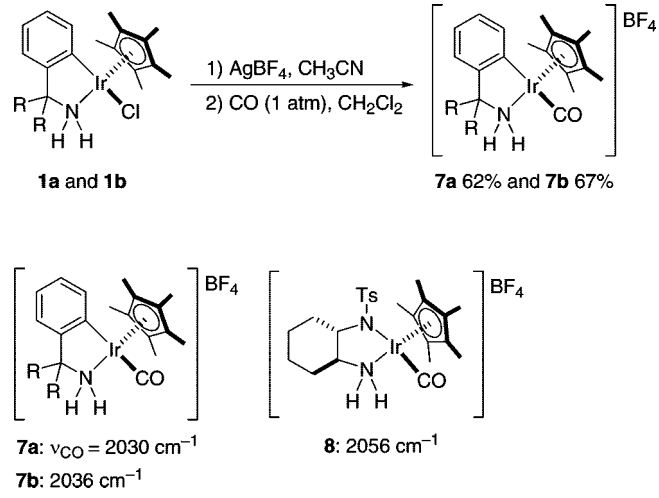
Figure 4. Molecular structure of $[Cp^*Ir[\kappa^2(N,C)$-$\{NH_2C(CH_3)_2$-2-$C_6H_4\}(CO)]BF_4$ (**7b**). Ellipsoids are shown at the 50% probability level for the non-hydrogen atoms.

complex **6b**, $Cp^*Ir(CH_2COCH_3)[\kappa^2(N,C)$-$\{NH_2C(CH_3)_2$-2-$C_6H_4\}]$, which was prepared by treatment of **2b** with an excess amount of acetone in 81% yield. The structure of the C-bound acetonyl complex was also confirmed by X-ray crystallography of **6b** depicted in Figure 3. An average distance of 2.824 Å for the $N(H_2)\cdots O{=}C$ motif indicates the presence of intramolecular hydrogen bonding.

Notably, the acetonyl 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 acetonyl 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 $Cp^*Ir[\kappa^2(N,N')$-$TsNCHC_6H_5CHC_6H_5NH]$, having $K_{eq} = 2.9 \times 10^{-2}$ 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 Cp^*Ir-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 $Cp^*Ir(Tscydn)CO$ complex **8** (cydn = 1,2-cyclohexanediamine) was similarly obtained. The molecular structure of the isolable

Scheme 4



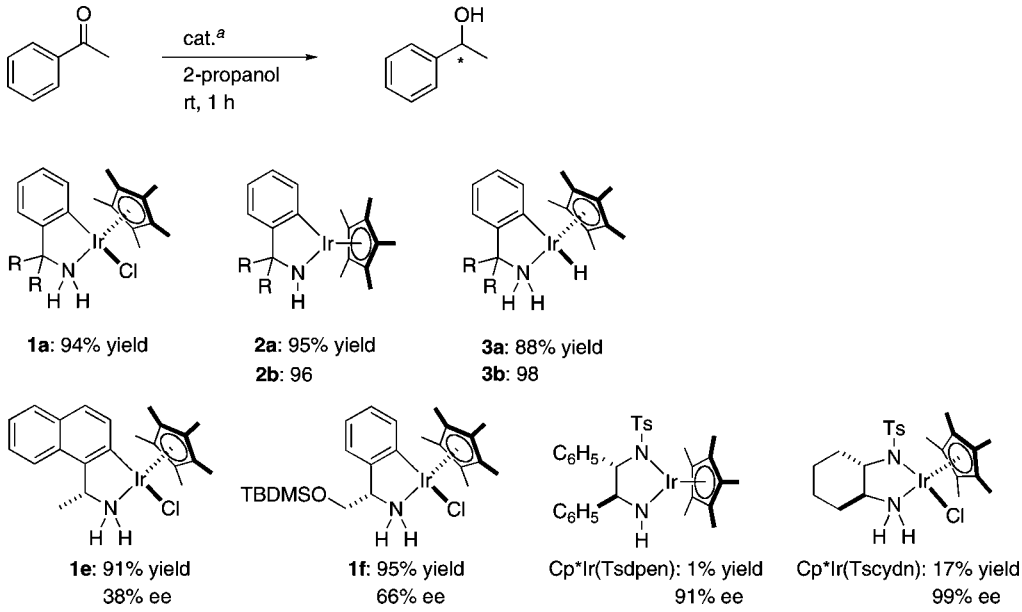
carbonyl complex **7b**, $[Cp^*Ir\{\kappa^2(N,C)$-$(NH_2C(CH_3)_2$-2-$C_6H_4)\}$-$(CO)]BF_4$, shown in Figure 4, confirmed that it has a three-legged piano stool configuration around the metal center and an Ir−CO distance of 1.855(3) Å.

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** ≃ **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

(17) Ito, M.; Ikariya, T. *Chem. Commun.* **2007**, 5134−5142.

Scheme 5[a]



[a] Catalysts **1** and Cp*Ir(Tscydn) required 1.2 equiv of $KOC(CH_3)_3$ 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*)-Tscydn 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 $KOC(CH_3)_3$ 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), P_2O_5 (dichloromethane, hexane, acetonitrile), or $CaSO_4$ (acetone) and distilled under argon. $[Cp^*IrCl_2]_2$,[18] $Cp^*Ir(OCOCH_3)_2$,[19] (*S*)-2-*tert*-butyldimethylsiloxy-1-phenylethylamine,[20] $Cp^*Ir[\kappa^2(N,N')$-(S,S)-$TsNCHC_6H_5CHC_6H_5NH]$,[2g] and $Cp^*IrCl[\kappa^2(N,N')$-(S,S)-Tscydn][2g] were prepared according to the literature. A deuterated alcohol, 3-pentanol-d_1, was prepared by reduction of 3-pentanone with $NaBD_4$. Other reagents were used as delivered. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL JNM-LA300 spectrometer and referenced to $SiMe_4$ via the solvent resonance. Elemental analyses were carried out using a PE2400 Series II CHNS/O analyzer (Perkin-Elemer). 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.[2g] Analytical gas chromatography was performed with a Shimadzu GC-17A gas chromatograph equipped with an Inert Cap Wax capillary column (0.25 mm × 30 m) purchased from GL Sciences Inc. Analytical chiral HPLC was performed on a Chiralcel OD column (4.6 mm × 25 cm) purchased from Daicel Chemical Industries, Ltd.

General Procedure for Synthesis of $Cp^*IrCl[\kappa^2(N,C)$-$(NH_2CR_2$-2-$C_6H_4)]$ (1a: R = C_6H_5, 1b: R = CH_3). A mixture of $[Cp^*IrCl_2]_2$ (0.1 g, 0.13 mmol), the appropriate benzylamine (0.25 mmol), and NaOAc (0.027 g, 0.33 mmol) in CH_2Cl_2 (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.

(18) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970–5977.
(19) Kang, J. W.; Maitlis, P. M. *J. Organomet. Chem.* **1971**, *30*, 127–133.
(20) Cheung, F. K.; Hayes, A. M.; Hannedouche, J.; Yim, A. S. Y.; Wills, M. *J. Org. Chem.* **2005**, *70*, 3188–3197.

Cp*IrCl[κ^2(*N*,*C*)-{$NH_2C(C_6H_5)_2$-2-C_6H_4}] (1a). Orange crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into the solution in CH_2Cl_2. Isolated yield: 76% (0.105 g, 0.17 mmol). ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.39 (s, 15H; $C(CH_3)_5$), 4.97, 5.72 (each d, $^2J_{HH}$ = 10 Hz, 1H; $NH_2C(C_6H_5)_2C_6H_4$), 6.22−7.58 (m, 14H; $NH_2C(C_6H_5)_2C_6H_4$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 8.4 ($C_5(CH_3)_5$), 80.5 ($NH_2C(C_6H_5)_2C_6H_4$), 88.4 ($C_5(CH_3)_5$), 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 ($NH_2C(C_6H_5)_2C_6H_4$). 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 $C_{29}H_{31}NClIr(CH_2Cl_2)_{0.5}$: C 53.39, H 4.86, N 2.11. Found: C 53.50, H 4.92, N 2.09.

Cp*IrCl[κ^2(*N*,*C*)-{$NH_2C(CH_3)_2$-2-C_6H_4}] (1b). Orange crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into the solution in CH_2Cl_2. Isolated yield: 79% (0.095 g, 0.19 mmol). ^{1}H NMR (300.4 MHz, $CDCl_3$, rt, δ/ppm): 1.21, 1.56 (each s, 3H; $NH_2C(CH_3)_2C_6H_4$), 1.70 (s, 15H; $C(CH_3)_5$), 3.88, 4.40 (each br, 1H; $NH_2C(CH_3)_2C_6H_4$), 6.79−6.86 (m, 2H; $NH_2C(CH_3)_2C_6H_4$), 6.91−6.97 (m, 1H; $NH_2C(CH_3)_2C_6H_4$), 7.42−7.45 (m, 1H; $NH_2C(CH_3)_2C_6H_4$). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$, rt, δ/ppm): 9.5 ($C_5(CH_3)_5$), 30.9, 32.0 ($NH_2C(CH_3)_2C_6H_4$), 66.5 ($NH_2C(CH_3)_2C_6H_4$), 87.0 ($C_5(CH_3)_5$), 121.4, 125.6, 127.1, 138.0, 154.2, 155.2 ($NH_2C(CH_3)_2C_6H_4$). 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 $C_{19}H_{27}NClIr$: 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[κ^2(*N*,*C*)-(NH_2CHR-2-Ar)] (1c: R = CH_3, 1d: R = H, 1e: (*R*)-1-(1-naphthyl)ethylamine, and 1f: (*S*)-2-*tert*-butyldimethylsiloxy-1-phenylethylamine). A mixture of $[Cp^*IrCl_2]_2$ (0.1 g, 0.13 mmol), the appropriate benzylamine (0.25 mmol), and NaOAc (0.027 g, 0.33 mmol) in CH_3CN (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[κ^2(*N*,*C*)-{$NH_2CH(CH_3)$-2-C_6H_4}] (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. ^{1}H NMR (300.4 MHz, $CDCl_3$, rt, δ/ppm): major diastereomer, 1.54 (d, $^3J_{HH}$ = 6.6 Hz, 1H; $NH_2CH(CH_3)C_6H_4$), 1.72 (s, 15H; $C(CH_3)_5$), 3.87 (m, 1H; $NH_2CH(CH_3)C_6H_4$), 3.77, 4.16 (each br, 1H; $NH_2CH(CH_3)C_6H_4$), 6.80−7.51 (4H; $NH_2CH(CH_3)C_6H_4$); minor diastereomer, 1.22 (d, $^3J_{HH}$ = 6.6 Hz, 1H; $NH_2CH(CH_3)C_6H_4$), 1.72 (s, 15H; $C(CH_3)_5$), 4.34 (m, 1H; $NH_2CH(CH_3)C_6H_4$), 3.51, 4.72 (each br, 1H; $NH_2CH(CH_3)C_6H_4$), 6.80−7.18 (m, 4H; $NH_2CH(CH_3)C_6H_4$). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$, rt, δ/ppm): major diastereomer, 9.3 ($C_5(CH_3)_5$), 22.8 ($NH_2CH(CH_3)C_6H_4$), 61.8 ($NH_2CH(CH_3)C_6H_4$), 86.4 ($C_5(CH_3)_5$), 121.3, 122.4, 127.7, 128.2, 129.0, 136.6 ($NH_2CH(CH_3)C_6H_4$); minor diastereomer, 9.4 ($C_5(CH_3)_5$), 24.7 ($NH_2CH(CH_3)C_6H_4$), 61.2 ($NH_2CH(CH_3)C_6H_4$), 86.6 ($C_5(CH_3)_5$), 119.2, 120.1, 125.3, 131.7, 136.2, 137.2 ($NH_2CH(CH_3)C_6H_4$). 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 $C_{18}H_{25}NClIr$: C 44.75, H 5.22, N 2.90. Found: C 44.72, H 5.51, N 2.65.

Cp*IrCl[κ^2(*N*,*C*)-(NH_2CH_2-2-C_6H_4)] (1d). Recrystallization from toluene and hexane afforded orange crystals. Isolated yield: 50% (0.092 g, 0.20 mmol). ^{1}H NMR (300.4 MHz, $CDCl_3$, rt, δ/ppm): 1.71 (s, 15H; $C(CH_3)_5$), 3.75−4.18 (4H; $NH_2CH_2C_6H_4$), 6.80−7.50 (m, 4H; $NH_2CH_2C_6H_4$). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$, rt, δ/ppm): 9.27 ($C_5(CH_3)_5$), 55.9 ($NH_2CH_2C_6H_4$), 86.4 ($C_5(CH_3)_5$), 120.1, 122.3, 127.2, 136.4, 146.5, 156.8 ($NH_2CH_2C_6H_4$). 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 $C_{17}H_{23}NClIr$: C 43.53, H 4.94, N 2.99. Found: C 43.17, H 4.93, N 2.95.

Cp*IrCl[κ^2(*N*,*C*)-(*R*)-{$NH_2CH(CH_3)$-2-$C_{10}H_6$}] (1e). Recrystallization from toluene and hexane afforded orange crystals. Isolated yield: 31% (0.047 g, 0.087 mmol). ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.54 (d, $^3J_{HH}$ = 7.5 Hz, 3H; $NH_2CH(CH_3)C_{10}H_6$), 1.62 (s, 15H; $C(CH_3)_5$), 2.12 (m, 1H; $NH_2CH(CH_3)C_{10}H_6$), 3.69, 4.82 (each br, 1H; $NH_2CH(CH_3)C_{10}H_6$), 7.14−7.76 (m, 6H; $NH_2CH(CH_3)C_{10}H_6$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 9.6 ($C_5(CH_3)_5$), 22.7 ($NH_2CH(CH_3)C_{10}H_6$), 59.7 ($NH_2CH(CH_3)C_{10}H_6$), 87.2 ($C_5(CH_3)_5$), 122.9, 123.7, 125.6, 126.2, 128.6, 131.4, 136.5, 146.0, 153.9 ($NH_2CH(CH_3)C_{10}H_6$). 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 $C_{22}H_{27}NClIr(C_6H_5CH_3)_{0.1}$: C 50.27, H 5.17, N 2.58. Found: C 50.07, H 5.21, N 2.20.

Cp*IrCl[κ^2(*N*,*C*)-(*S*)-{$NH_2CH(CH_2OSi(CH_3)_2{}^tBu)$-2-$C_6H_4$}] (1f). Recrystallization from diethyl ether afforded orange crystals. Isolated yield: 35% (0.25 g, 0.4 mmol). ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 0.12, 0.16 (each s, 3H; $OSi(CH_3)_2C(CH_3)_3$), 0.75 (s, 9H; $OSi(CH_3)_2C(CH_3)_3$), 1.72 (s, 15H; $C(CH_3)_5$), 3.03 (m, 1H; NH_2CH), 3.64, 4.13 (each m, 1H; CH_2), 4.39, 4.71 (each br, 1H; NH_2), 6.78−7.46 (m, 4H; C_6H_4). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 8.5 ($C(CH_3)_3$), 9.3 ($C_5(CH_3)_5$), 18.3 ($OSi(CH_3)_2(C(CH_3)_3$), 26.0 ($C(CH_3)_3$), 65.7 (CH_2), 68.3 (NH_2CH), 87.0 ($C_5(CH_3)_5$), 120.9, 122.3, 127.4, 137.2, 148.4, 156.5 (C_6H_4). 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 $C_{24}H_{39}NOClIrSi$: 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[κ^2(*N*,*C*)-($NHCR_2$-2-Ar)] (2a: R = C_6H_5, 2b: R = CH_3, and 2e: (*R*)-1-(1-naphthyl)-ethylamine). A mixture of Cp*IrCl[κ^2(*N*,*C*)-NH_2CR_2-2-Ar] (0.35 mmol) and dry $KOC(CH_3)_3$ (0.53 mmol) in CH_2Cl_2 (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[κ^2(*N*,*C*)-{$NHC(C_6H_5)_2$-2-C_6H_4}] (2a). Recrystallization from a concentrated solution in diethyl ether afforded purple crystals. Isolated yield: 80% (0.16 g, 0.28 mmol). ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.95 (s, 15H; $C(CH_3)_5$), 6.81−8.09 (m, 14H; $NHC(C_6H_5)_2C_6H_4$), 8.00 (br, 1H; $NHC(C_6H_5)_2C_6H_4$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 10.0 ($C_5(CH_3)_5$), 87.3 ($NHC(C_6H_5)_2C_6H_4$), 90.9 ($C_5(CH_3)_5$), 122.6, 124.3, 125.0, 126.3, 127.6, 127.8, 136.8, 145.4, 160.7, 164.5 ($NHC(C_6H_5)_2C_6H_4$). 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 $C_{29}H_{30}NIr$: C 59.56, H 5.17, N 2.40. Found: C 59.53, H 5.36, N 2.05.

Cp*Ir[κ^2(*N*,*C*)-{$NHC(CH_3)_2$-2-C_6H_4}] (2b). Recrystallization from a concentrated solution in diethyl ether afforded purple crystals. Isolated yield: 88% (0.10 g, 0.22 mmol). ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.32 (s, 6H; $NHC(CH_3)_2C_6H_4$), 1.94 (s, 15H; $C(CH_3)_5$), 6.82−6.96 (m, 2H; $NHC(CH_3)_2C_6H_4$), 7.13 (d, $^3J_{HH}$ = 7.3 Hz, 1H; $NHC(CH_3)_2C_6H_4$), 8.02 (d, $^3J_{HH}$ = 7.3 Hz, 1H; $NHC(CH_3)_2C_6H_4$), 8.47 (br, 1H; $NHC(CH_3)_2C_6H_4$) ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 10.4 ($C_5(CH_3)_5$), 27.9 ($NHC(CH_3)_2C_6H_4$), 78.9 ($NHC(CH_3)_2C_6H_4$), 87.1 ($C_5(CH_3)_5$), 120.8, 122.6, 125.1, 136.8, 162.1, 163.3 ($NHC(CH_3)_2C_6H_4$). 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 $C_{19}H_{26}NIr$: C 49.54, H 5.69, N 3.04. Found: C 49.45, H 5.72, N 2.92.

Cp*Ir[κ^2(*N*,*C*)-(*R*)-{$NHCH(CH_3)$-2-$C_{10}H_6$}] (2e). Recrystallization from diethyl ether afforded purple crystals. Isolated yield: 63% (0.083 g, 0.17 mmol). ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.48 (d, $^3J_{HH}$ = 4.5 Hz, 3H; $NHCH(CH_3)C_{10}H_6$), 1.97 (s, 15H; $C(CH_3)_5$), 2.91 (m, 1H; $NHCH(CH_3)C_{10}H_6$), 7.22−8.28 (m, 6H; $NHCH(CH_3)C_{10}H_6$), 8.42 (br, 1H; $NHCH(CH_3)C_{10}H_6$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 9.5 ($C_5(CH_3)_5$), 21.8 ($NHCH(CH_3)C_{10}H_6$), 74.5 ($NHCH(CH_3)C_{10}H_6$), 87.7 ($C_5(CH_3)_5$),

123.1, 124.6, 125.2, 125.3, 128.3, 128.6, 131.5, 136.0, 155.8, 162.5 ($NHC(CH_3)_2C_{10}H_6$). 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 $C_{22}H_{26}NIr$: 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[κ^2(*N,C*)-(NH_2CR_2-2-C_6H_4)] (3a: R = C_6H_5, 3b: R = CH_3). Cp*Ir[κ^2(*N,C*)-($NHCR_2$-2-C_6H_4)] (**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[κ^2(*N,C*)-{$NH_2C(C_6H_5)_2$-2-C_6H_4}] (3a). Isolated yield: 88% (0.23 g, 0.39 mmol). ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): −12.92 (s, 1H; Ir*H*), 1.84 (s, 15H; C(CH_3)$_5$), 4.33, 5.78 (each br, 1H; NH_2C(C_6H_5)$_2$$C_6H_4$), 6.63−7.45 (m, 14H; $NH_2C(C_6H_5)_2C_6H_4$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 9.9 ($C_5(CH_3)_5$), 80.3 ($NH_2C(C_6H_5)_2C_6H_4$), 87.4 ($C_5(CH_3)_5$), 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 ($NH_2C(C_6H_5)_2C_6H_4$). 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 $C_{29}H_{32}NIr$: C 59.36, H 5.50, N 2.39. Found: C 59.33, H 5.59, N 2.20.

Cp*IrH[κ^2(*N,C*)-{$NH_2C(CH_3)_2$-2-C_6H_4}] (3b). Isolated yield: 86% (0.27 g, 0.59 mmol). ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): −13.23 (s, 1H; Ir*H*), 1.27, 1.48 (each s, 3H; $NH_2C(CH_3)_2C_6H_4$), 1.93 (s, 15H; C(CH_3)$_5$), 3.21, 4.47 (each br, 1H; NH_2C(CH_3)$_2$$C_6H_4$), 6.62 (d, $^3J_{HH}$ = 7.3 Hz, 1H; $NH_2C(CH_3)_2C_6H_4$), 6.72 (t, $^3J_{HH}$ = 7.3 Hz, 1H; $NH_2C(CH_3)_2C_6H_4$), 6.79 (t, $^3J_{HH}$ = 7.3 Hz, 1H; $NH_2C(CH_3)_2C_6H_4$), 7.32 (d, $^3J_{HH}$ = 7.3 Hz, 1H; $NH_2C(CH_3)_2C_6H_4$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 9.4 ($C_5(CH_3)_5$), 28.8, 30.9 ($NH_2C(CH_3)_2C_6H_4$), 66.9 ($NH_2C(CH_3)_2C_6H_4$), 87.2 ($C_5(CH_3)_5$), 117.4, 118.2, 120.3, 120.6, 126.1, 137.3 ($NH_2C(CH_3)_2C_6H_4$). 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 $C_{19}H_{28}NIr$: C 49.33, H 6.10, N 3.03. Found: C 49.11, H 6.13, N 3.04.

Synthesis of Cp*IrD[κ^2(*N,C*)-{$NH_2C(CH_3)_2$-2-C_6H_4}] (3b-D). $C_2H_5CD(OH)C_2H_5$ (0.031 mL, 0.28 mmol) was added to a solution of Cp*Ir[κ^2(*N,C*)-{$NHC(CH_3)_2$-2-C_6H_4}] (**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). ^{1}H NMR (300.4 MHz, THF-d_8, rt, δ/ppm): 1.12, 1.64 (each s, 3H; $NH_2C(CH_3)_2C_6H_4$), 1.70 (s, 15H; C(CH_3)$_5$), 4.38, 4.92 (each br, 1H; NH_2C(CH_3)$_2$$C_6H_4$), 6.67 (d, $^3J_{HH}$ = 4.6 Hz, 1H; $NH_2C(CH_3)_2C_6H_4$), 6.75−6.81 (m, 2H; $NH_2C(CH_3)_2C_6H_4$), 7.35 (d, $^3J_{HH}$ = 7.3 Hz, 1H; $NH_2C(CH_3)_2C_6H_4$). ^{2}H NMR (46.1 MHz, THF, rt, δ/ppm): −13.34 (s. 1H: Ir-*D*).

Synthesis of Cp*Ir($OCOCH_3$)[κ^2(*N,C*)-{$NH_2C(C_6H_5)_2$-2-C_6H_4}] (4). Method A: Acetic acid (0.010 mL, 0.14 mmol) was added to a solution of Cp*Ir[κ^2(*N,C*)-{$NHC(C_6H_5)_2$-2-C_6H_4}] (**2a**) (0.084 g, 0.14 mmol) in CH_2Cl_2 (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($OCOCH_3$)$_2$ (0.15 g, 0.30 mmol) and triphenylmethylamine (0.078 g, 0.30 mmol) in CH_2Cl_2 (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). ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.36 (s, 15H; C(CH_3)$_5$), 1.91 (s, 3H; OCOCH_3), 4.85, 8.51 (each br, 1H; NH_2C(C_6H_5)$_2$$C_6H_4$), 6.26−7.77 (m, 14H; $NH_2C(C_6H_5)_2C_6H_4$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 8.98 ($C_5(CH_3)_5$), 25.7 (OCO*C*H_3), 79.9 ($NH_2C(C_6H_5)_2C_6H_4$), 85.9 ($C_5(CH_3)_5$), 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 ($NH_2C(C_6H_5)_2C_6H_4$), 180.6 (O*C*OCH$_3$). 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 $C_{31}H_{34}NO_2Ir$: 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[$CH(COOCH_3)_2$][κ^2(*N,C*)-{$NH_2C(C_6H_5)_2$-2-C_6H_4}] (5). Dimethyl malonate (0.031 mL, 0.27 mmol) was added to a solution of Cp*Ir[κ^2(*N,C*)-{$NHC(C_6H_5)_2$-2-C_6H_4}] (**2a**) (0.158 g, 0.27 mmol) in CH_2Cl_2 (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). ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.30 (s, 15H; C(CH_3)$_5$), 2.80, 3.60 (each s, 3H; COOCH_3), 4.09 (s, 1H; IrC*H*), 4.33, 7.19 (each br, 1H; NH_2C(C_6H_5)$_2$$C_6H_4$), 6.30−7.52 (m, 14H; $NH_2C(C_6H_5)_2C_6H_4$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 8.5 ($C_5(CH_3)_5$), 49.8, 50.6 (COO*C*H$_3$), 59.8 (Ir*C*H), 80.5 ($NH_2C(C_6H_5)_2C_6H_4$), 88.4 ($C_5(CH_3)_5$), 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 ($NH_2C(C_6H_5)_2C_6H_4$), 175.3, 177.7 (*C*OOCH$_3$). 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 $C_{34}H_{38}NO_4Ir$: 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(CH_2COCH_3)[κ^2(*N,C*)-(NH_2CR_2-2-C_6H_4)] (6a: R = C_6H_5, 6b: R = CH_3). A solution of Cp*Ir[κ^2(*N,C*)-($NHCR_2$-2-C_6H_4)] (**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(CH_2COCH_3)[κ^2(*N,C*)-{$NH_2C(C_6H_5)_2$-2-C_6H_4}] (6a). Isolated yield: 87% (0.086 g, 0.13 mmol). ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.36 (s, 15H; C(CH_3)$_5$), 1.99 (s, 3H; IrCH$_2$COCH_3), 2.27, 3.00 (each d, $^2J_{HH}$ = 5.9 Hz, 1H; IrCH_2COCH$_3$), 4.40, 6.80 (each br, 1H; NH_2C(C_6H_5)$_2$$C_6H_4$), 6.18−7.35 (m, 14H; $NH_2C(C_6H_5)_2C_6H_4$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 8.8 ($C_5(CH_3)_5$), 17.8 (CH_2COCH_3), 29.5 (CH_2COCH_3), 81.1 ($NH_2C(C_6H_5)_2C_6H_4$), 87.2 ($C_5(CH_3)_5$), 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 ($NH_2C(C_6H_5)_2C_6H_4$), 213.8 (*C*O). 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 $C_{32}H_{36}NOIr$: C 59.79, H 5.64, N 2.18. Found: C 59.61, H 5.91, N 1.86.

Cp*Ir(CH_2COCH_3)[κ^2(*N,C*)-{$NH_2C(CH_3)_2$-2-C_6H_4}] (6b). Isolated yield: 81% (0.063 g, 0.12 mmol). ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.27, 1.46 (each s, 3H; $NH_2C(CH_3)_2C_6H_4$), 1.65 (s, 3H; IrCH$_2$COCH_3), 1.70 (s, 15H; C(CH_3)$_5$), 2.55 (AB pattern, $^2J_{HH}$ = 9.1 Hz, 2H; IrCH_2COCH$_3$), 3.12, 5.57 (each br, 1H; NH_2C(CH_3)$_2$$C_6H_4$), 6.63−6.72 (m, 2H; $NH_2C(CH_3)_2C_6H_4$), 6.79−6.85 (m, 1H; $NH_2C(CH_3)_2C_6H_4$), 7.18−7.21 (m, 1H; $NH_2C(CH_3)_2C_6H_4$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 9.1 ($C_5(CH_3)_5$), 15.3 (CH_2COCH_3), 30.7 (CH_2COCH_3), 30.2, 32.4 ($NH_2C(CH_3)_2C_6H_4$), 66.6 ($NH_2C(CH_3)_2C_6H_4$), 86.8 ($C_5(CH_3)_5$), 121.1, 121.3, 126.6, 136.6, 152.7, 155.1 ($NH_2C(CH_3)_2C_6H_4$), 216.9 (*C*O). 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 $C_{22}H_{32}NOIr$: 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)[κ^2(*N,C*)-{NH_2CR_2-2-C_6H_4}](BF_4) (7a: R = C_6H_5, 7b: R = CH_3) and [Cp*Ir{κ^2(*N,N′*)-(*S,S*)-Tscydn}(CO)]BF_4 (8). To an acetonitrile solution (8 mL) of the chloride complex Cp*IrCl[κ^2(*N,C*)-(NH_2CR_2-2-C_6H_4)] (**1**) or Cp*IrCl[κ^2(*N,N′*)-(*S,S*)-Tscydn][2g] (0.15 mmol) was added $AgBF_4$ (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 CH_2Cl_2. After bubbling of CO gas (0.1 MPa) into the reaction mixture for 30 min, the

Table 1. Crystallographic Data for 2a, 4, 6b, and7b

	2a	4	6b	7b
empirical formula	$C_{29}H_{30}IrN$	$C_{31}H_{34}IrNO_2$	$C_{22}H_{32}IrN$	$C_{20}H_{27}BF_4IrNO$
fw	584.78	644.84	518.72	576.46
cryst color	purple	orange	yellow	colorless
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P\bar{1}$ (#2)	$P2_1/c$ (#14)
a, Å	7.870(3)	10.922(4)	9.092(4)	8.626(3)
b, Å	10.155(4)	19.511(7)	9.101(5)	15.356(5)
c, 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)	
V, Å^3	1166.9(8)	2689.8(17)	2038.7(17)	2146.3(12)
Z	2	4	4	4
D_{calcd}, g cm^{-3}	1.664	1.592	1.690	1.784
F_{000}	576.00	1280.00	1024.00	1120.00
μ, cm^{-1} (Mo Kα)	57.528	50.048	65.763	62.813
exposure rate, sec/°	6.0	2.0	2.0	10.0
no. of reflections measured	8570	20929	15937	16276
nol of unique reflections	4916	6118	8888	4845
no. variables	310	398	521	286
R_1 ($I > 2.00\sigma(I)$)[a]	0.0249	0.0377	0.0373	0.0431
wR_2 (all reflections)[a]	0.0654	0.0913	0.1014	0.1122
GOF on F^2	0.999	1.000	1.001	1.001

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, w$R_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$.

solvent was evaporated under vacuum. Recrystallization from CH_2Cl_2 and hexane afforded colorless crystals.

[Cp*Ir{κ²(*N*,*C*)-(NH₂C(C₆H₅)₂-2-C₆H₄)}(CO)]BF₄ (7a). Isolated yield: 62% (0.067 g, 0.090 mmol). ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.78 (s, 15H; C(C*H*$_3$)$_5$), 5.15, 6.65 (each br, 1H; N*H*$_2$C(C$_6$H$_5$)$_2$C$_6$H$_4$), 6.40−7.45 (m, 14H; NH$_2$C(C$_6$*H*$_5$)$_2$C$_6$*H*$_4$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 8.7 (C$_5$(*C*H$_3$)$_5$), 81.3 (*C*$_5$(CH$_3$)$_5$), 100.7 (NH$_2$*C*(C$_6$H$_5$)$_2$C$_6$H$_4$), 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 (NH$_2$C(*C*$_6$H$_5$)$_2$*C*$_6$H$_4$), 168.3 (Ir*C*O). 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[κ²(*N*,*C*)-{NH₂C(CH₃)₂-2-C₆H₄}(CO)]BF₄ (7b). Isolated yield: 67% (0.064 g, 0.10 mmol). ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.50, 1.61 (each s, 3H; NH$_2$C(C*H*$_3$)$_2$C$_6$H$_4$), 2.01 (s, 15H; C(C*H*$_3$)$_5$), 4.46, 5.38 (each br, 1H; N*H*$_2$C(CH$_3$)$_2$C$_6$H$_4$), 6.85 (d, $^3J_{HH}$ = 7.1 Hz, 1H; NH$_2$C(CH$_3$)$_2$C$_6$*H*$_4$), 7.05−7.15 (m, 2H; NH$_2$C(CH$_3$)$_2$C$_6$*H*$_4$), 7.23 (d, $^3J_{HH}$ = 7.1 Hz, 1H; NH$_2$C(CH$_3$)$_2$C$_6$*H*$_4$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 9.1 (C$_5$(*C*H$_3$)$_5$), 29.3, 30.8 (NH$_2$C(*C*H$_3$)$_2$C$_6$H$_4$), 68.9 (*C*$_5$(CH$_3$)$_5$), 100.8 (NH$_2$*C*-(CH$_3$)$_2$C$_6$H$_4$), 123.4, 126.0, 128.2, 131.9, 136.3, 157.2 (NH$_2$C(CH$_3$)$_2$*C*$_6$H$_4$), 168.7 (Ir*C*O). 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{κ²(*N*,*N*′)-(*S*,*S*)-Tscydn}(CO)]BF₄ (8). Isolated yield: 57% (0.053 g, 0.075 mmol). ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.97 (s, 15H; C(C*H*$_3$)$_5$), 2.23 (s, 3H; SO$_2$C$_6$H$_4$C*H*$_3$), 0.512.72 (m, 10H, N(C$_6$H$_{10}$)NH$_2$), 4.63, 4.93 (each br, 2H, N(C$_6$H$_{10}$)N*H*$_2$), 7.29, 7.69 (each d, J = 7.8 Hz, J = 8.1 Hz SO$_2$C$_6$*H*$_4$CH$_3$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 9.4 (C$_5$(*C*H$_3$)$_5$), 21.6, 24.7, 25.0, 34.6, 34.8, 67.4, 69.4 ((*C*$_6$H$_{10}$)NH$_2$, SO$_2$C$_6$H$_4$*C*H$_3$), 101.8 (*C*$_5$(CH$_3$)$_5$), 127.9, 129.9, 138.6, 143.3, 167.7 (SO$_2$*C*$_6$H$_4$CH$_3$), 194.0 (Ir*C*O). 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 Kα 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.

Acknowledgment. This work was financially supported by a grant-in-aid from the Ministry of Education, Science, Sports and Culture of Japan (No. 12305057, 14078209) and partially supported by The 21st Century COE Program.

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.

OM800124F