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Synthesis and Reactivity of Bis(protic N-heterocyclic carbene)iridium(III) Complexes

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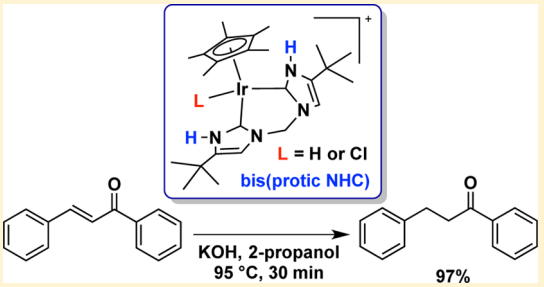
Supporting Information

ABSTRACT: A nonfunctionalized bis(imidazole) ligand precursor has been directly metalated using IrCp*$(OAc)_2$, leading to a mixture of bis(protic N-heterocyclic carbene) (bisPNHC) complexes (**2a**,**b**). Treatment of **2a**,**b** with HCl gas in CH_2Cl_2 gave a bisPNHC complex (**3a**), which has been transformed into a hydride bisPNHC complex. Complex **3a** underwent ligand and counterion exchange reactions to afford acetonitrile and ethylamine bisPNHC complexes (**5** and **6**). Furthermore, these bisPNHC complexes have been tested as catalysts in transfer hydrogenation reactions of ketones and unsaturated ketones.



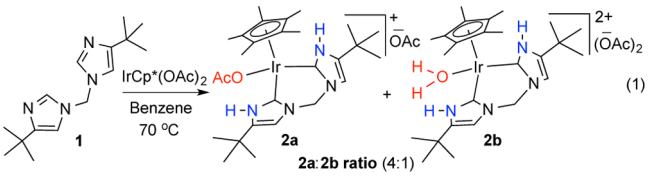
INTRODUCTION

N-heterocyclic carbenes (NHCs) are well-known ancillary ligands that provide important properties to a coordinated metal center in terms of stability and/or activation, mainly due to NHC steric and electronic factors.[1] During the past decade, an increasing number of protic NHC (PNHC) complexes have been reported.[2] In contrast to typical NHCs, PNHCs could act as reactive ligands activating and/or recognizing substrates by hydrogen bonding.[3] However, PNHC complexes have been scarcely studied due to their more difficult synthesis, since the reaction of an imidazole with a metal tends to give an N-coordinated tautomer instead of a PNHC complex.[4] Relatively few methods of syntheses have been reported, and a more limited number of articles relate to PNHC reactivity and catalysis.[5]

In general, the syntheses of PNHCs require more than one step,[5g,6] with the use of acids,[7] bases,[5h,8] other reagents,[9] or donor-functionalized azoles.[5a,b,d−f,10] With donor-functionalized azoles, where the PNHC is obtained by tautomerization, to the best of our knowledge, there are only two reports on bisPNHC complexes that have been synthesized by this method.[5a,10e] A facile way to synthesize PNHC complexes could lead to a better understanding of these compounds, especially their potential bifunctional behavior. Here we report a one-pot synthesis of a facially oriented bisPNHC complex by direct metalation starting with a nonfunctionalized bis(imidazole) (**1**), as well as its reactivity and catalytic activity in transfer hydrogenation.

RESULTS AND DISCUSSION

The equimolar reaction of **1** with IrCp*$(OAc)_2$ in benzene at 70 °C led to CH activation, giving two species according to NMR spectra (eq 1). The isolated product (51% total yield) was analyzed by ^{1}H NMR spectroscopy in CD_2Cl_2 and D_2O,



(1)

giving signals for two species with a ratio of 4:1. This reaction was also carried out in toluene and THF with similar results. The observed Ir−C signals by $^{13}C\{^1H\}$ NMR at δ 152.2 and 151.5 are consistent with protic carbene formation in both species. The major species is **2a**, which shows a weak and broad NH signal at δ 12.46 and an AB system of diastereotopic CH_2 hydrogens (J = 12.8 Hz). However, the analysis of **2a**,**b** by HRMS (ESI-TOF) showed only **2a** with a peak at m/z 647.2929 amu.

The structure of **2b** was proposed to have two acetate counterions and a coordinated aquo ligand, the presence of which is most likely due to the hygroscopic nature of IrCp*$(OAc)_2$ instead of the sensitivity of **2a** to the presence of water. Rather surprisingly, a control experiment in which the 4:1 mixture of **2a** and **2b** was treated with water (2.6 equiv, $CDCl_3$, 70 °C, 20 h) did not increase the amount of **2b**.

The crystallization of the crude product led to a sample containing two species with a similar ratio according to NMR

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spectra. Interestingly, X-ray diffraction analysis showed the structure of **2b**, with a three-legged piano-stool geometry around the metal center. The two PNHC ligands and aquo ligand are the legs (Figure 1). The cationic complex and two

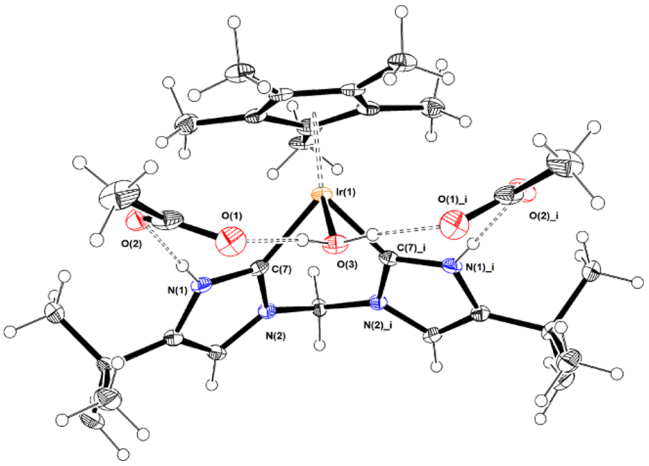
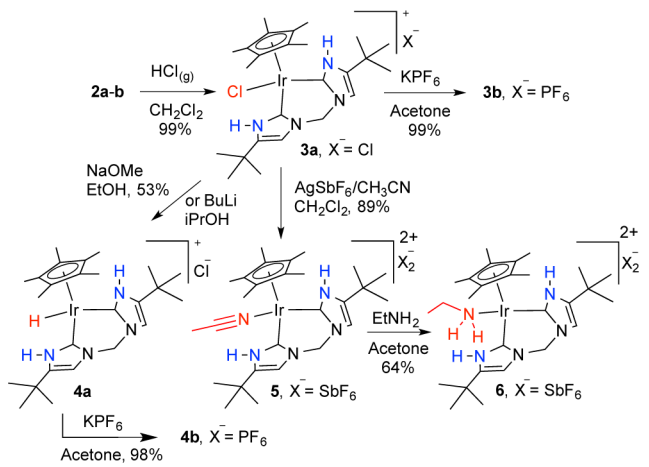


Figure 1. Molecular structure of bisPNHC complex **2b**. Thermal ellipsoids are set at 35% probability.

acetate anions are held together by four hydrogen bonds from N−H of the bidentate carbene and O−H of the aquo ligand to acetate counterions (N−H···O = 1.884(4) Å and O−H···O = 1.792(7) Å). Both hydrogen bond geometries are nearly linear with angles of 177.2(5) and 165.9(1)°.

Treatment of a solution with the mixture of **2a** and **2b** with HCl(g) led to the formation of bisPNHC(Cl) complex **3a** in 99% yield, which can also be obtained in a one-step synthesis by bubbling HCl(g) briefly into the reaction mixture from **1** and $IrCp^*(OAc)_2$ in CH_2Cl_2 (Scheme 1). The ^1H and ^{13}C

Scheme 1. Synthesis and Reactivity of BisPNHC Complexes



NMR spectra of **3a** in CD_3CN showed resonances for one species, with downfield shifts of the NH and the carbene carbon at δ 11.02 and 151.9, respectively. In order to increase the solubility of **3a** in less polar solvents, the chloride counterion was exchanged for hexafluorophosphate by reacting a suspension of **3a** with KPF_6 to afford the bisPNHC(PF_6) complex **3b**.

Complex **3a** reacts with NaOMe in ethanol through a β-hydride elimination to give the hydride **4a**. Reaction of **3a** with BuLi in 2-propanol also gives **4a**, although with a lower yield (40%). The ^1H NMR spectra of **4a** in CD_3CN showed the characteristic resonances of an NH (δ 10.73, sl br) and a hydride (δ −15.89, sl br). In addition, the protons of the Cp* presented a coupling with the hydride atom (2.04 ppm, d, $^4J_{HH}$ = 0.6 Hz) and the ^{13}C NMR spectra showed the resonance for the carbene carbon at 150.5 ppm. The counterion exchange reaction of colorless complex **4a** with potassium hexafluorophosphate afforded **4b** in 98% yield. The NH and the hydride ^1H NMR resonances in acetone-d_6 (δ 11.15 and −15.77 ppm, respectively) are slightly shifted to lower field in comparison with data for **4a**.

Suitable crystals of **4a** for X-ray diffraction were obtained by vapor diffusion of hexanes into a concentrated solution of **4a** in a mixture of acetonitrile/dichloromethane. The molecular structure shows the same geometry around the iridium atom observed in complex **2b**, with a hydride, Cp*, and bisPNHC ligand coordinated to the metal center. Both carbene C−Ir bonds showed equivalent distances of 2.003(5) Å, which are slightly shorter than those in **2b** (2.017(5) Å). The outer-sphere chloride ion presents a hydrogen bond interaction with the NH wingtip in the asymmetric unit (Figure 2).

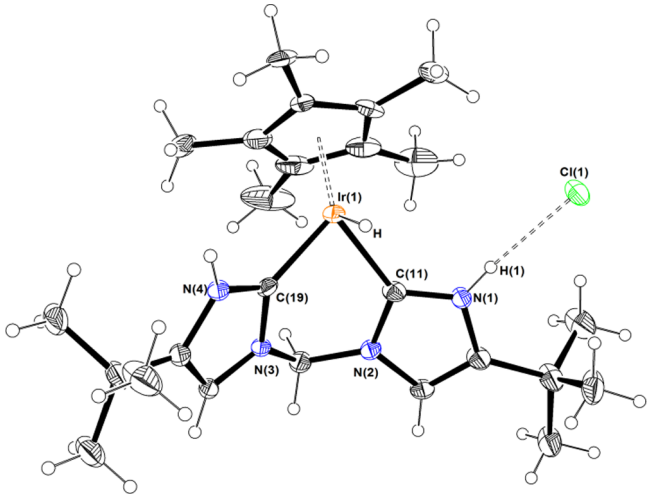


Figure 2. Molecular structure of bisPNHC complex **4a**. Thermal ellipsoids are set at 30% probability.

Reactivity studies on **3a** showed that both chlorides can be removed using $AgSbF_6$ in the presence of acetonitrile. Treatment of a solution of **3a** in CH_2Cl_2 with $AgSbF_6$ deepens the initial yellow color to orange, and when acetonitrile is added, the reaction mixture turns colorless instantaneously and the reaction goes to completion within minutes to give complex **5**. The ^1H spectrum of **5** showed the presence of an NH group and a singlet for the methyl of the coordinated acetonitrile (δ 12.07 and 2.70 ppm, respectively). Complex **5** was treated with ethylamine in acetone at room temperature, giving **6** according to ^1H NMR spectra. The resonances for the ethylamine ligand appear as a multiplet and a triplet (δ 2.30 and 1.01 ppm, respectively), whereas the resonance for the NH_2 protons appears as a broad singlet at 4.46 ppm.

We also report results of transfer hydrogenation reactions with complexes **3a**,**b**. Reduction of acetophenone was carried out at 95 °C in 2-propanol-d_8 and KOH as base. Complexes **3a**,**b** showed similar catalytic activities, giving conversions of 96 and 98% in 24 h, respectively (Table 1, entries 1 and 2). In

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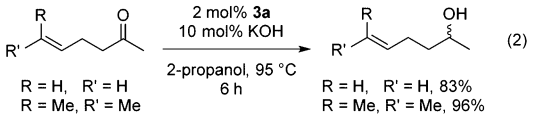
Table 1. Reduction of Acetophenone by 3a,b

entry	complex	temp (°C)	time (h)	yield (%)[a]
1	**3a**	95	24	96
2	**3b**	95	24	98
3	**3b**	70	139	96
4		95	24	41

[a]Conversions were determined with mesitylene as the internal standard for NMR analysis.

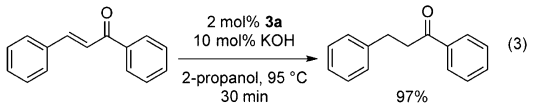
contrast, a longer reaction time is necessary when the catalysis is performed at 70 °C (entry 3). A control experiment, carried out in the absence of **3a** or **3b**, showed that the base itself mediates the transfer hydrogenation of acetophenone, although with a much lower conversion (entry 4).

Furthermore, complex **3a** was tested as a catalyst in the transfer hydrogenation of alkenones (eq 2). Analysis by GC-



(2)

MS indicated that the carbonyl group of alkenones can be selectively hydrogenated within 6 h. An increase in the reaction time for 5-hexen-2-one led to isomerization products. In contrast, isomerization did not occur when 6-methyl-5-hepten-2-one was hydrogenated, probably due to the sterics of the methyl substituents. Moreover, the hydrogenation of an α,β-unsaturated ketone ((*E*)-chalcone) by **3a** was selective for the double bond and required only 30 min to give 97% yield (eq 3). After this time, hydrogenation of the carbonyl group gave



(3)

the saturated alcohol product in 63% yield in 24 h. Control experiments for the transfer hydrogenation of 5-hexen-2-one, 6-methyl-5-hepten-2-one, and (*E*)-chalcone were carried out under the same reaction conditions of eqs 2 and 3 but in the absence of complex **3a**. Analysis by GC-MS showed that the hydrogenation is also selective but with much lower conversions (10, 12, and 12%, respectively).

Complexes **3b** and **4a,b** were also used for the conjugate reduction. Surprisingly, hydride complexes **4a,b** needed a base to hydrogenate and their reactivity was comparable with their analogues **3a,b**, which indicates that there is not a counterion effect on the catalytic activity for these bisPNHC Ir(III) complexes. In addition, the fast chemoselective transfer hydrogenation could be favored by the ability of the bisPNHC complexes to participate in hydrogen bonding with alkenones as substrates.

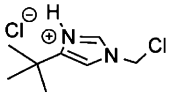
CONCLUSIONS

In summary, we have synthesized iridium(III) complexes **2a,b** featuring two facially oriented PNHC ligands by direct metalation using a nonfunctionalized imidazole. The appropriate choice of imidazole *tert*-butyl substituent and reactivity of the acetate-bearing starting material allowed *formation of two PNHC ligands without any extra reagent in a one-pot synthesis*. The reactivity of **2a,b** led to the formation of bisPNHC complex **3a**, which can be converted into **3b** or **5** by counterion and ligand exchange reactions. Moreover, complex **3a** reacts with NaOMe in ethanol or LiOiPr in 2-propanol to give hydride complex **4a** by β-hydride elimination. Complex **5** contains a labile ligand in its structure that reacts with ethylamine to give **6**. Complex **3a** shows promising use as a bifunctional catalyst for selective hydrogenation of the carbonyl group of nonconjugated alkene−ketones, whereas with an α,β-unsaturated ketone, the hydrogenation is selective for the double bond. Additional reactivity studies and applications in other types of catalytic reactions are in progress.

EXPERIMENTAL SECTION

General Procedures. Unless otherwise specified, all manipulations were carried out in a nitrogen-filled glovebox or using Schlenk techniques. Commercially available reagents were used as received from Aldrich Chemical Co. and Alfa Aesar. $[IrCp^*Cl_2]_2$[11] and $IrCp^*(OAc)_2$[12] were prepared by published procedures. $CDCl_3$ was purchased from Cambridge Isotope Laboratories (CIL), dried over calcium hydride, and vacuum-transferred prior to use. CD_3CN, $(CD_3)_2CO$, and CD_2Cl_2 were used as received from CIL. NMR spectra were recorded at 400 MHz with a Bruker Avance III spectrometer at 30 °C unless otherwise specified. ^1H and ^{13}C NMR chemical shifts are reported in ppm referenced to residual solvent resonances (^1H NMR, 7.24 ppm for $CHCl_3$ in $CDCl_3$, 5.32 ppm for $CHDCl_2$ in CD_2Cl_2, 7.16 ppm for C_6HD_5 in C_6D_6, 1.94 ppm for CHD_2CN in CD_3CN, 2.05 ppm for acetone-d_5 in acetone-d_6; $^{13}C\{^1H\}$ NMR, 77.23, 128.39, 1.39, and 29.92 ppm for chloroform-d_1, benzene-d_6, acetonitrile-d_3, and acetone-d_6, respectively). Coupling constants J are given in hertz (Hz). IR spectra were recorded on a PerkinElmer FT-IR 1605 spectrophotometer (ATR mode). Melting points were measured in an Electrothermal GAC 88629 apparatus. Mass spectra were obtained by direct insertion on an Agilent Technologies 5975C instrument . High-resolution mass spectrometry (HRMS) data were obtained with a micrOTOF-Q III MS instrument with electrospray ionization using sodium formate as calibrant. Elemental analyses were performed at NuMega Resonance Laboratories, San Diego, CA. Satisfactory microanalytical data for **3a** and **4a,b** could not be obtained since complex **3a** is hygroscopic and hydrides **4a,b** are air sensitive. Hence, a complete set of NMR and HRMS spectra is provided in the Supporting Information. X-ray diffraction data for crystals of complexes were collected on a Bruker APEX II CCD diffractometer.

Synthesis of 4-(*tert*-Butyl)-1-(chloromethyl)-1*H*-imidazole Hydrochloride.



In air, 4-(*tert*-butyl)-1*H*-imidazole[13] (1.2480 g, 10.05 mmol) and 1.3 mL of an aqueous 37% solution of formaldehyde were dissolved in methanol and the mixture was refluxed for 3 h. The mixture was concentrated in vacuo and triturated with acetone (3 × 8 mL), giving a pale yellow solid. White crystals were obtained at −18 °C by slow diffusion of ethyl ether into a concentrated solution of (4-(*tert*-butyl)-1*H*-imidazol-1-yl)methanol in acetone: yield 1.4928 g (9.6803 mmol, 96%); mp 100−103 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.52 (br s, 1H, OH), 6.96 (d, 1H, $^4J_{HH}$ = 1.2 Hz, H-2), 6.81 (d, 1H, $^4J_{HH}$ = 1.2 Hz, H-5), 5.30 (s, 2H, CH_2OH), 1.21 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 152.7 (C-4), 135.5 (C-2), 112.6 (C-5), 70.6 (NCH_2OH), 31.9 ($C(CH_3)_3$), 30.2 ($C(CH_3)_3$). EI-MS m/z (%): 154 (M^+, 6), 139 (27), 124 (43), 109 (100), 41 (39), 39 (41). Anal. Calcd for $C_8H_{14}N_2O$ (154.20): C, 62.31; H, 9.15; N, 18.17. Found: C, 62.45; H, 9.19; N, 18.10. At 0 °C, thionyl chloride was added dropwise (1.1593 g, 9.7444 mmol) to a solution of (4-(*tert*-butyl)-1*H*-imidazol-1-yl)methanol (1.4878 g, 9.6479 mmol) in dry dichloromethane (22 mL) and the reaction mixture was stirred for 40 min. After it was warmed to room temperature and stirred for 2 h, the mixture was concentrated under reduced pressure. The residue was triturated with anhydrous ethyl ether (3 × 8 mL). The product was obtained as a

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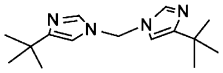
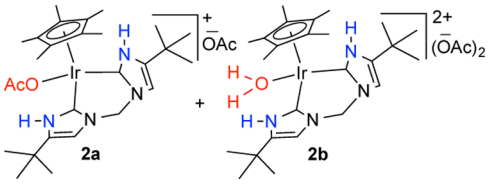
viscous yellow oil and was used without further purification: yield 1.9562 g (9.3543 mmol, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.67 (br s, 1H, NH), 10.15 (s, 1H, H-2), 6.96 (s, 1H, H-5), 6.20 (s, 2H, CH_2Cl), 1.40 (s, 9H, $C(CH_3)_3$). ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 146.1 (C-4), 137.3 (C-2), 114.4 (C-5), 54.4 (NCH_2Cl), 31.6 ($C(CH_3)_3$), 29.5 ($C(CH_3)_3$). EI-MS m/z (%): 172 (M^+, 27), 156 (100), 137 (29), 121 (29), 108 (18), 95 (7).

Synthesis of 1.



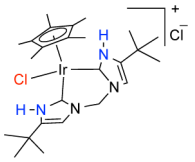
4-(*tert*-Butyl)-1*H*-imidazole (2.2800 g, 18.3602 mmol) was dissolved in dry DMF (10 mL) and added dropwise at 0 °C to a solution of NaH (950.8 mg, 37.6384 mmol) in dry DMF (15 mL). After it was warmed to room temperature and stirred for an additional 30 min, the mixture was cooled to 0 °C and a solution of 4-(*tert*-butyl)-1-(chloromethyl)-1*H*-imidazole hydrochloride (4.0314 g, 19.2782 mmol) in dry DMF (15 mL) was slowly added. The mixture was stirred overnight at room temperature. The reaction was quenched with water (42 mL), and the aqueous phase was extracted with dichloromethane (40 mL). The organic phase was washed with water (3 × 42 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting orange residue was dissolved with ethyl ether and stored at −18 °C. White crystals were obtained, washed with cold ethyl ether, and vacuum-dried: yield 1.9522 g (7.4976 mmol, 41%); mp 188−191 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, 2H, $^4J_{HH}$ = 1.2 Hz, H-2), 6.63 (d, 2H, $^4J_{HH}$ = 1.2 Hz, H-5), 5.80 (s, 2H, NCH_2N), 1.23 (s, 18H, $C(CH_3)_3$). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 154.7 (C-4), 136.0 (C-2), 111.9 (C-5), 56.5 (NCH_2N), 32.0 ($C(CH_3)_3$), 30.2 ($C(CH_3)_3$). EI-MS m/z (%): 260 (M^+, 33), 245 (100), 189 (8), 137 (76). HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{15}H_{25}N_4$ 261.2074; found 261.2066. Anal. Calcd for $C_{15}H_{24}N_4$ (260.37): C, 69.19; H, 9.29; N, 21.52. Found: C, 68.89; H, 9.05; N, 21.32.

Synthesis of 2a,b.



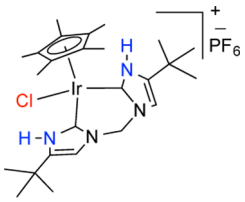
A mixture of bis(4-(*tert*-butyl)-1*H*-imidazol-1-yl)methane (250.0 mg, 0.9613 mmol) and IrCp*$(OAc)_2$ (427.5 mg, 0.9601 mmol) was dissolved in benzene (5 mL) with stirring at 70 °C for 24 h. After the mixture was cooled to room temperature, the solvent was removed under vacuum. The brown residue was dissolved in dry THF and dichloromethane and crystallized by vapor diffusion of hexanes, giving a 4:1 mixture of the complexes as yellow crystals: yield 345.6 mg (0.3917 mmol, 41% **2a**, 0.0955 mmol, 10% **2b**). IR (ATR, cm^{-1}): 3427 ν(N−H). ^{1}H NMR (400 MHz, CD_2Cl_2): **2a** δ 12.46 (br s, 2H, NH), 7.01 (s, 2H, H-5), 6.27 (d, 1H, $^2J_{HH}$ = 12.8 Hz, NCH_2N), 5.45 (d, 1H, $^2J_{HH}$ = 12.8 Hz, NCH_2N), 1.96 (s, 3H, $OOCCH_3$), 1.85 (s, 3H, $OOCCH_3$), 1.76 (s, 15H, $C_5(CH_3)_5$), 1.31 (s, 18H, $C(CH_3)_3$); **2b** δ 15.98 (br s, 2H, NH), 6.77 (s, 2H, H-5), 5.84 (d, 1H, $^2J_{HH}$ = 12.8 Hz, NCH_2N), 5.50 (d, 1H, $^2J_{HH}$ = 12.8 Hz, NCH_2N), 1.96 (s, 6H, $OOCCH_3$), 1.79 (s, 15H, $C_5(CH_3)_5$), 1.31 (s, 18H, $C(CH_3)_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): **2a** δ 180.8 ($OOCCH_3$), 176.3 ($OOCCH_3$), 152.2 (C-2), 144.9 (C-4), 115.1 (C-5), 92.2 ($C_5(CH_3)_5$), 61.7 (NCH_2N), 31.1 ($C(CH_3)_3$), 29.6 ($C(CH_3)_3$), 24.2 (2C, $OOCCH_3$), 10.0 ($C_5(CH_3)_5$). HRMS (ESI-TOF) m/z: [M$^+$] calcd for $C_{27}H_{42}N_4O_2Ir$ (**2a**) 647.2933; found 647.2929. Complex **2b** was not detected by HRMS.

Synthesis of 3a.



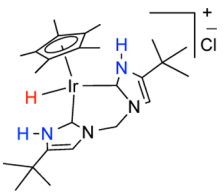
A mixture of bis(4-(*tert*-butyl)-1*H*-imidazol-1-yl)methane (250.0 mg, 0.9613 mmol) and IrCp*$(OAc)_2$ (427.5 mg, 0.9601 mmol) was dissolved in benzene (5 mL) with stirring at 70 °C for 24 h. After the mixture was cooled to room temperature, the solvent was removed under vacuum. The brown residue was dissolved in dichloromethane (8 mL), and hydrogen chloride was bubbled for 3.5 min. The solvent was removed under reduced pressure, the residue was triturated with ethyl ether (5 × 4 mL), and the volatile components were evaporated. The yellow solid was vacuum-dried over 1 week until no more acetic acid was present. The resulting solid was dissolved in chloroform and stored at −18 °C for 24 h. A microcrystalline yellow solid was decanted, washed with cold chloroform, and vacuum-dried: yield 346.5 mg (0.5260 mmol, 55%); mp 247−250 °C. IR (ATR, cm^{-1}): 3411 ν(N−H). ^{1}H NMR (400 MHz, CD_3CN): δ 11.02 (br s, 2H, NH), 7.01 (d, 2H, $^4J_{HH}$ = 2.0 Hz, H-5), 6.15 (d, 1H, $^2J_{HH}$ = 13.0 Hz, NCH_2N), 5.48 (d, 1H, $^2J_{HH}$ = 13.0 Hz, NCH_2N), 1.82 (s, 15H, $C_5(CH_3)_5$), 1.27 (s, 18H, $C(CH_3)_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CD_3CN): δ 151.9 (C-2), 144.9 (C-4), 115.8 (C-5), 94.1 ($C_5(CH_3)_5$), 62.2 (NCH_2N), 31.6 ($C(CH_3)_3$), 29.4 ($C(CH_3)_3$), 9.9 ($C_5(CH_3)_5$). HRMS (ESI-TOF) m/z: [M$^+$] calcd for $C_{25}H_{39}N_4ClIr$ 623.2479; found 623.2497. Anal. Calcd for $C_{25}H_{39}N_4Cl_2Ir + 3H_2O$ (712.77): C, 42.13; H, 6.36; N, 7.86. Found: C, 42.05; H, 6.50; N, 7.87. As complex **3a** was highly hygroscopic, all purification attempts were unsuccessful.

Synthesis of 3b.



Complex **3a** (100.0 mg, 0.1518 mmol) and an excess of KPF_6 (85.5 mg, 0.4554 mmol) were dissolved in acetone (2.5 mL). The reaction mixture was stirred for 30 min. The suspension was filtered through a plug of Celite and concentrated under reduced pressure. The yellow residue was dissolved in dichloromethane (2 mL) and filtered. Yellow crystals were obtained at ambient temperature by vapor diffusion of hexanes into concentrated solution of the complex in dichloromethane: yield 115.3 mg (0.1501 mmol, 99%); mp 284−288 °C. IR (ATR, cm^{-1}): 3463 ν(N−H). ^{1}H NMR [400 MHz, $(CD_3)_2CO$]: δ 11.56 (br s, 2H, NH), 7.14 (s, 2H, H-5), 6.23 (d, 1H, $^2J_{HH}$ = 13.2 Hz, NCH_2N), 5.78 (d, 1H, $^2J_{HH}$ = 13.2 Hz, NCH_2N), 1.83 (s, 15H, $C_5(CH_3)_5$), 1.24 (s, 18H, $C(CH_3)_3$). ^{13}C {^{1}H} NMR (100.6 MHz, $(CD_3)_2CO$): δ 151.2 (C-2), 144.3 (C-4), 115.6 (C-5), 93.6 ($C_5(CH_3)_5$), 61.9 (NCH_2N), 31.1 ($C(CH_3)_3$), 28.9 ($C(CH_3)_3$), 9.2 ($C_5(CH_3)_5$). ^{31}P {^{1}H} NMR (161.9 MHz, $(CD_3)_2CO$): δ −144.3 (sept, J_{PF} = 705.9 Hz). HRMS (ESI-TOF) m/z: [M$^+$] calcd for $C_{25}H_{39}N_4ClIr$ 623.2479; found 623.2480. Anal. Calcd for $C_{25}H_{39}N_4ClIrPF_6$ (768.23): C, 39.09; H, 5.12; N, 7.29. Found: C, 38.75; H, 4.94; N, 7.09.

Synthesis of 4a.



This complex can be synthesized by either reaction of **3a** (50.0 mg, 0.0759 mmol) with BuLi in 2-propanol at room temperature (yield 40%) or from the reaction of **3a** with NaOMe. Complex **3a** (50.0 mg,

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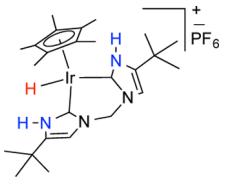
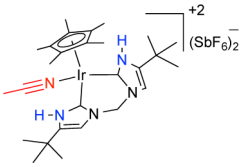
0.0759 mmol) and NaOMe (4.1 mg, 0.0759 mmol) were dissolved in deoxygenated ethanol (1.5 mL). The reaction mixture was stirred for 6 h at room temperature. The suspension was filtered through a plug of Celite and concentrated under reduced pressure. The residue was triturated with dichloromethane (1.5 mL) and decanted. The white solid was redissolved in acetonitrile and filtered. Colorless crystals were obtained at ambient temperature by vapor diffusion of hexanes into a concentrated solution of the complex in a dichloromethane/acetonitrile mixture: yield 25.2 mg (0.0403 mmol, 53%). ^{1}H NMR (400 MHz, CD_3CN): δ 10.73 (br s, 2H, NH), 6.87 (d, 2H, $^4J_{HH}$ = 1.9 Hz, H-5), 5.75 (d, 1H, $^2J_{HH}$ = 12.7 Hz, NCH_2N), 5.34 (d, 1H, $^2J_{HH}$ = 12.7 Hz, NCH_2N), 2.04 (d, 15H, $^4J_{HH}$ = 0.6 Hz, $C_5(CH_3)_5$), 1.28 (s, 18H, $C(CH_3)_3$), −15.89 (br s, 1H, IrH). A cross peak between the NH and residual water was observed in the 2D EXSY NMR spectrum, which is a consequence of an exchange process involving the NH of both PNHCs and residual water. Exchange between both NHs and [Ir]-H could not be determined due to the insolubility of **4a** in nonpolar NMR solvents. ^{13}C{^{1}H} NMR (100.6 MHz, CD_3CN): δ 150.5 (C-2), 143.7 (C-4), 114.7 (C-5), 93.3 ($C_5(CH_3)_5$), 62.6 (NCH_2N), 31.3 ($C(CH_3)_3$), 29.5 ($C(CH_3)_3$), 10.8 ($C_5(CH_3)_5$). HRMS (ESI-TOF) m/z: [M$^+$] calcd for $C_{25}H_{40}N_4Ir$ 589.2878; found 589.2880. Anal. Calcd for $C_{25}H_{40}N_4ClIr$ (624.29): C, 48.10; H, 6.46; N, 8.97. Found: C, 49.09; H, 6.80; N, 9.07. Although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date.

Synthesis of 4b.



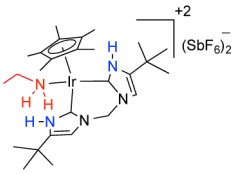
Complex **4b** was prepared in the same manner as **3b**, using **4a** (15.0 mg, 0.024 mmol) and KPF_6 (13.5 mg, 0.072 mmol) in acetone/2-propanol. After filtration, the white solid was washed with dichloromethane and dried in vacuo: yield 17.3 mg (0.023 mmol, 98%). ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 11.15 (br s, 2H, NH), 7.10 (d, 2H, $^4J_{HH}$ = 1.6 Hz, H-5), 6.10 (d, 1H, $^2J_{HH}$ = 12.8 Hz, NCH_2N), 5.62 (d, 1H, $^2J_{HH}$ = 12.8 Hz, NCH_2N), 2.02 (s, 15H, $C_5(CH_3)_5$), 1.30 (s, 18H, $C(CH_3)_3$), −15.77 (br s, 1H, IrH). ^{13}C{^{1}H} NMR (100.6 MHz, $(CD_3)_2CO$): δ 149.5 (C-2), 142.7 (C-4), 114.4 (C-5), 92.4 ($C_5(CH_3)_5$), 61.9 (NCH_2N), 30.5 ($C(CH_3)_3$), 28.8 ($C(CH_3)_3$), 9.9 ($C_5(CH_3)_5$). ^{31}P {^{1}H} NMR (161.9 MHz, $(CD_3)_2CO$): δ −144.3 (sept, J_{PF} = 707.5 Hz). HRMS (ESI-TOF) m/z: [M$^+$] calcd for $C_{25}H_{40}N_4Ir$ 589.2878; found 589.2888.

Synthesis of 5.



$AgSbF_6$ (15.9 mg, 0.0456 mmol) was added to a stirred solution of **3a** (15.0 mg, 0.0228 mmol) in dichloromethane at room temperature. After 1 h, acetonitrile (75 μL, 1.4 mmol) was added dropwise until the reaction mixture became colorless. The suspension was filtered and concentrated under reduced pressure. Dichloromethane (3 × 1 mL) and hexanes (1 × 1 mL) were added and then removed under high vacuum to afford a pale pink solid: yield 22.3 mg (0.0202 mmol, 89%). ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 12.07 (br s, 2H, NH), 7.40 (d, 2H, $^4J_{HH}$ = 2.0 Hz, H-5), 6.51 (d, 1H, $^2J_{HH}$ = 13.8 Hz, NCH_2N), 6.01 (d, 1H, $^2J_{HH}$ = 13.8 Hz, NCH_2N), 2.70 (s, 3H, CH_3CN), 1.97 (s, 15H, $C_5(CH_3)_5$), 1.35 (s, 18H, $C(CH_3)_3$). ^{13}C {^{1}H} NMR (100.6 MHz, $(CD_3)_2CO$): δ 145.8 (C-4), 144.6 (C-2), 121.3 (CH_3CN), 117.6 (C-5), 96.4 ($C_5(CH_3)_5$), 63.0 (NCH_2N), 31.7 ($C(CH_3)_3$), 29.5 ($C(CH_3)_3$), 9.7 ($C_5(CH_3)_5$), 3.9 (CH_3CN). HRMS (ESI-TOF) m/z: [M^{2+}] calcd for $C_{27}H_{42}N_5Ir$ 314.6530; found 314.6520. Anal. Calcd for $C_{27}H_{42}N_5IrSb_2F_{12}$ (1100.37): C, 29.47; H, 3.85; N, 6.36. Found: C, 29.32; H, 4.05; N, 6.42.

Synthesis of 6.



Complex **5** (15.0 mg, 0.0136 mmol) was treated with ethylamine (27 μL, 2.0 M) in acetone-d_6 at room temperature. The reaction mixture was concentrated under reduced pressure, and the residue was triturated with dichloromethane and ethyl ether. In air, the white solid obtained was suspended in dichloromethane and filtered through a plug of Celite. The white solid was recovered with acetone and vacuum-dried: yield 9.6 mg (0.0087 mmol, 64%). We note that the appearance of triplets for the ethylamine carbons ($^2J_{CD}$ = 11.5 Hz and $^3J_{CD}$ = 4.5 Hz) can be taken as evidence that the NH_2 undergoes an H/D exchange process with traces of HOD in the NMR solvent to form the monodeuterated amine ligand CH_3CH_2NHD. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 11.74 (br s, 2H, NH), 7.40 (s, 2H, H-5), 6.49 (d, 1H, $^2J_{HH}$ = 13.4 Hz, NCH_2N), 6.04 (d, 1H, $^2J_{HH}$ = 13.4 Hz, NCH_2N), 4.46 (br s, 1H, NHD), 2.36 (m, 2H, CH_3CH_2NHD), 1.92 (s, 15H, $C_5(CH_3)_5$), 1.35 (s, 18H, $C(CH_3)_3$), 1.00 (t, 3H, $^3J_{HH}$ = 7.0 Hz, CH_3CH_2NHD). ^{13}C{^{1}H} NMR (100.6 MHz, $(CD_3)_2CO$): δ 147.4 (C-2), 145.3 (C-4), 117.4 (C-5), 94.4 ($C_5(CH_3)_5$), 62.8 (NCH_2N), 45.2 (t, $^2J_{CD}$ = 11.5 Hz, CH_3CH_2NHD), 31.5 ($C(CH_3)_3$), 29.5 ($C(CH_3)_3$), 17.9 (t, $^3J_{CD}$ = 4.5 Hz, CH_3CH_2NHD), 9.6 ($C_5(CH_3)_5$). Complex **6** was also analyzed in acetone-d_6 containing less HOD. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 11.61 (br s, 2H, NH), 7.41 (s, 2H, H-5), 6.50 (d, 1H, $^2J_{HH}$ = 13.2 Hz, NCH_2N), 6.06 (d, 1H, $^2J_{HH}$ = 13.6 Hz, NCH_2N), 4.45 (br s, 2H, NH_2), 2.31 (m, 2H, $CH_3CH_2NH_2$), 1.92 (s, 15H, $C_5(CH_3)_5$), 1.35 (s, 18H, $C(CH_3)_3$), 1.03 (t, 3H, $^3J_{HH}$ = 7.2 Hz, $CH_3CH_2NH_2$). ^{13}C {^{1}H} NMR (100.6 MHz, $(CD_3)_2CO$): δ 147.6 (C-2), 145.4 (C-4), 117.6 (C-5), 94.6 ($C_5(CH_3)_5$), 63.0 (NCH_2N), 45.5 ($CH_3CH_2NH_2$), 31.6 ($C(CH_3)_3$), 29.6 ($C(CH_3)_3$), 18.1 ($CH_3CH_2NH_2$), 9.7 ($C_5(CH_3)_5$). Anal. Calcd for $C_{27}H_{46}N_5IrSb_2F_{12}$ (1104.40): C, 29.36; H, 4.20; N, 6.34. Found: C, 29.51; H, 3.92; N, 6.16.

General Procedure for Transfer Hydrogenation Studies Monitored by ^{1}H NMR. Acetophenone (0.06 mmol), 1,3,5-trimethylbenzene (2 μL) as internal standard, and 0.6 mL of 2-propanol-d_8 were transferred into a J. Young NMR tube, and a ^{1}H NMR spectrum was recorded. Then, the precatalyst (2 mol %) and KOH (10 mol %) were added. The reaction mixture was heated at 95 °C for 24 h. The conversions were quantified by the integration of the ^{1}H NMR signals of the alcohol and acetophenone. The value of the integral for the singlet due to the aromatic protons of 1,3,5-trimethylbenzene (internal standard) was set to 10 units in each case.

General Procedure for Transfer Hydrogenation Studies Monitored by Gas Chromatography−Mass Spectrometry (GC-MS). *Alkenones.* 6-Methyl-5-hepten-2-one or 5-hexen-2-one (0.1 mmol) and precatalyst (2 mol %) were stirred in 2-propanol (1 mL) in a 2 mL vial at 70 °C for 1 h. Then KOH (10 mol %) was added and the mixture was stirred at 95 °C for 6 h. An aliquot (0.1 mL) was taken and diluted to 1 mL with 2-propanol.

α,β-Unsaturated Ketones. To a 2-propanol solution (1 mL) of (*E*)-chalcone (0.1 mmol) in a 2 mL vial were added the precatalyst (2 mol %) and KOH (10 mol %). Then the mixture was stirred at 95 °C for 30 min. An aliquot (0.1 mL) was taken and diluted to 1 mL with 2-propanol.

The analytical GC/MS system used was an Agilent 7890A GC coupled to an Agilent Technologies 5975C mass detector, equipped with a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm). An Agilent Technologies 7693 autosampler was used to inject 1 μL of a solution sample. The ionization energy was 70 eV with a mass range of 30−800 m/z. The temperature of the injector was set at 250 °C and that of the detector to 230 °C. The flow rate of the carrier gas (helium) was 1.0 mL/min injected with a gas dilution of 1:50.

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Identification of the individual components was based on comparison with the mass spectra library (NIST98). For the substrate 5-hexen-2-one the initial temperature of the column was set at 60 °C, held for 2 min, and then a ramp of 10 °C/min to 250 °C was used. For the substrate 6-methylhept-5-en-2-one the initial temperature of the column was set at 70 °C, held for 2 min, and then a ramp of 10 °C/min to 250 °C was used. For the substrate (*E*)-chalcone the initial temperature of the column was set at 80 °C, held for 2 min, and then a ramp of 10 °C/min to 250 °C was used.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00501.

Nuclear magnetic resonance spectra for all complexes, GC-MS analysis, HRMS spectra and crystallographic data for complexes **2b** and **4a** (PDF)

X-ray crystallographic files for complexes **2b** and **4a** (CIF)

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Notes

The authors declare no competing financial interest.

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