Pyridine-Based N-Heterocyclic Carbene Hydride Complexes of Iridium via C−H Activation

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A series of iridium(III) hydride complexes of chelating pyridine-based N-heterocyclic carbenes (py-NHCs) and remote N-heterocyclic carbenes (remote py-NHCs) were synthesized as stable products from the C−H oxidative addition reactions of pyridine-tethered pyridinium halides and $[Ir(COD)_2]^+$. X-ray crystal structures of representative iridium py-NHC and remote py-NHC complexes were determined and in all cases mutual *cis* orientations of the halide and hydride ligands were observed in the solid state. In the solution phase, the *cis* isomer was observed as the only product for each iridium(III) py-NHC complex, whereas both *cis* and *trans* isomers have been observed as equilibration mixtures for iridium(III) remote py-NHC complexes. No β-insertion of the hydride into a C═C bond of the COD unit of iridium(III) py-NHC hydride complexes was observed, and theoretical studies indicate that this step is thermodynamically unfavorable. Iridium(III) py-NHC hydride complexes have shown high catalytic activity in transfer hydrogenation of ketone and enones. Computational studies of the donor capacity of those ligands indicate that py-NHCs are more donating than imidazole-derived NHCs.

Introduction

Ever since the isolation of imidazole-based carbenes in the free state,[1] N-heterocyclic carbenes (NHCs) have become powerful ligands to stabilize transition metals in organometallic chemistry and in catalysis.[2−4] The high catalytic activities of NHC complexes may be attributed to the strong σ-donating and weak π-accepting characters of imidazole-2-ylidenes.[5,6] As typical electron-rich carbon-centered neutral donors, NHCs on various platforms and with different substituents have been developed to demonstrate their electronic and steric tenability.[7,8] In addition to the normal imidazole-derived NHCs, the "abnormal" carbenes, first discovered by Crabtree and co-workers,[9] which have a carbenoid center adjacent to only one nitrogen, have proven to be more donating than the normal ones.[10,11] Analogous to abnormal NHCs, NHCs derived from the deprotonation of pyridiniums at the 2- position are also stabilized by only one nitrogen atom (Figure 1). Previous experimental and theoretical studies have shown that pyridine-based NHCs (py-NHCs) are generally stronger σ-donors and π-acceptors than the more common imidazole-2-ylidenes,[12,13] although examples of py-NHC complexes are still rather limited. More recently,

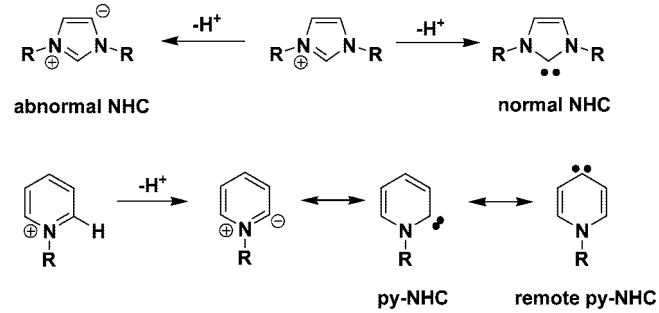

Figure 1. NHCs, abnormal NHCs, py-NHCs, and remote py-NHCs.

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remote N-heterocylic carbenes derived from pyridine,[14] quinoline,[15] or pyrazoline,[16] where the heteroatom is distal to the carbene carbon (Figure 1), have received increasing attention owing to their unique structures and properties. For instance, Raubenheimer et al. have reported that palladium remote py-NHC complexes are more active in catalyzing C−C coupling reactions than their imidazole-2-ylidenes analogues.[17]

In comparison to imidazoliums, pyridiniums are much less acidic, which renders their metalation more difficult and thus examples of py-NHC complexes are rather limited. Common methods to access py-NHC complexes include (i) C-halogen oxidative addition of 2- or 4-halopyridiums when treated with low valent transition metals such as Pd[14,15,18] or Pt,[19] (ii) quaternization of iridium or rhodium pyridyl complexes,[20] (iii) metalation of in situ generated carbenes from the deprotonation of pyridiniums by strong bases,[12] and (iv) C−H oxidative addition of functionalized pyridiniums.[21] Kinetic studies of the π-accepting ability of these complexes showed distinctive *trans*-labilizing ability of these py-NHCs in ligand substitution reactions.[21]

Metalation of pyridiums via a C−H activation route might be an advantageous method owing to base-free reaction conditions. We now report the synthesis of a series of iridium(III) hydride complexes stabilized by chelating py-NHCs or remote py-NHCs via intramolecular C−H activation under mild conditions. The catalytic activities of representative complexes in transfer hydrogenation of ketones and computational assessment of the donating ability of such ligands have also been studied.

Results and Discussions

Ligand System. We[22] and others[23] have recently reported Ir(I)-mediated intramolecular C−H activation of functionalized imidazoliums to afford iridium(III) NHC hydride complexes. We have also described Ir(I)-induced tautomerization of 2,3-bipyridyls to the corresponding NHCs, a process that involes the activation of the C2−H bond of those pyridium uints.[24] We reason that pyridium ions tethered to pyridinium moieties (**1**−**4,** Figure 2) should be more reactive toward C−H activation in that *ortho* C-H activation should be favored by chelation assistance and the products are chelation-stabilized NHC complexes. We thus synthesized compounds **1**−**4** as carbene precursors from the selective alkylation of the corresponding heterocycles in high yields.

C−H Activation of Compound 1. We have chosen $[Ir(COD)_2]SbF_6$ or $[Ir(COD)_2]PF_6$ as a metal source owing to the lability of one of the COD (1,5-cyclooctadiene) ligands.[24] Compound **1** (Figure 2) was allowed to react with 1 equiv of $[Ir(COD)_2]SbF_6$ in dichloromethane at room temperature, and two hydride species were obtained based on ^{1}H NMR analysis. These two hydrides resonate at δ −12.9 (s) and −14.3 (s) in a 1:5 ratio. In the ^{13}C NMR spectrum, two corresponding Ir−$C_{carbene}$ signals were detected at δ 187.5 and 178.3. The structures of these two products, however, could not be securely assigned because four possible isomers, two regio- (py-NHC or remote py-NHC) and two stereoisomers (*trans* or *cis* orientation of the hydride and the iodide), can be possible.

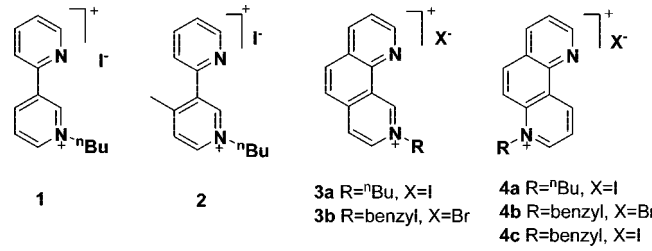
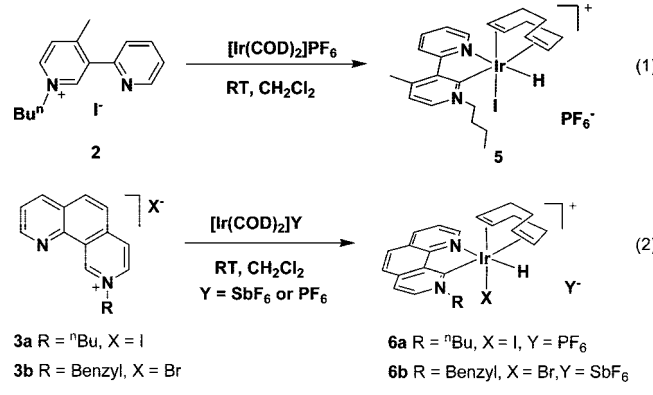


Figure 2. Pyridine-tethered pyridinium halides.

Table 1. Characteristic NMR Signals (CD_2Cl_2) of Iridium Hydride Complexes 5−7

	5	6a	6b	7a	7b	7c
Ir-*H*	−13.52	−13.79	−12.96	−14.13 (*cis*) −12.81 (*trans*)	−13.61 (*cis*) −14.01 (*trans*)	−14.11 (*cis*) −12.62 (*trans*)
Ir-$C_{carbene}$	182.5	189.6	189.7	191.1 (*cis*)	192.1 (*cis*) 191.9 (*trans*)	192.5 (*cis*)

C−H Activation of Ligands with Blocking Groups. To enhance the selectively of C−H activation of this system, ligands **2** and **3a**,**b** with blocking groups (Figure 2) were used as carbene precursors so that only one *ortho* C-H bond could be activated. Stirring a solution of **2** or **3a,b** and $[Ir(COD)_2]PF_6$ or $[Ir(COD)_2]SbF_6$ (CH_2Cl_2, 25 °C) led to the decolorization of the solution. With the liberation of 1 equiv of COD, the reaction yielded complex **5** or **6a,b**, respectively, as the only product in 65−96% isolated yields (eqs 1 and 2). These products have been fully characterized by NMR spectroscopy (Table 1), and **5** and **6b** were further characterized as *cis* hydride iodide complexes by X-ray crystallography (vide infra). The hydrides of complexes **5** and **6a,b** resonate within a range of δ −12.96 to −13.79 in the ^{1}H NMR spectra (CD_2Cl_2), and the Ir−$C_{carbene}$ signals appear within a range of δ 182.5 to 189.7 in the ^{13}C NMR spectra (Table 1). These ^{13}C NMR data are comparable to those reported for other py-NHC complexes.[21,24]



Unfavorable β-H Insertion Reaction. The hydride, the iridium, and either of the C═C bonds of the COD ligand adopt a *syn* coplanar conformation on the basis of the X-ray crystal structures of complex **5**, an orientation necessary for β-hydride

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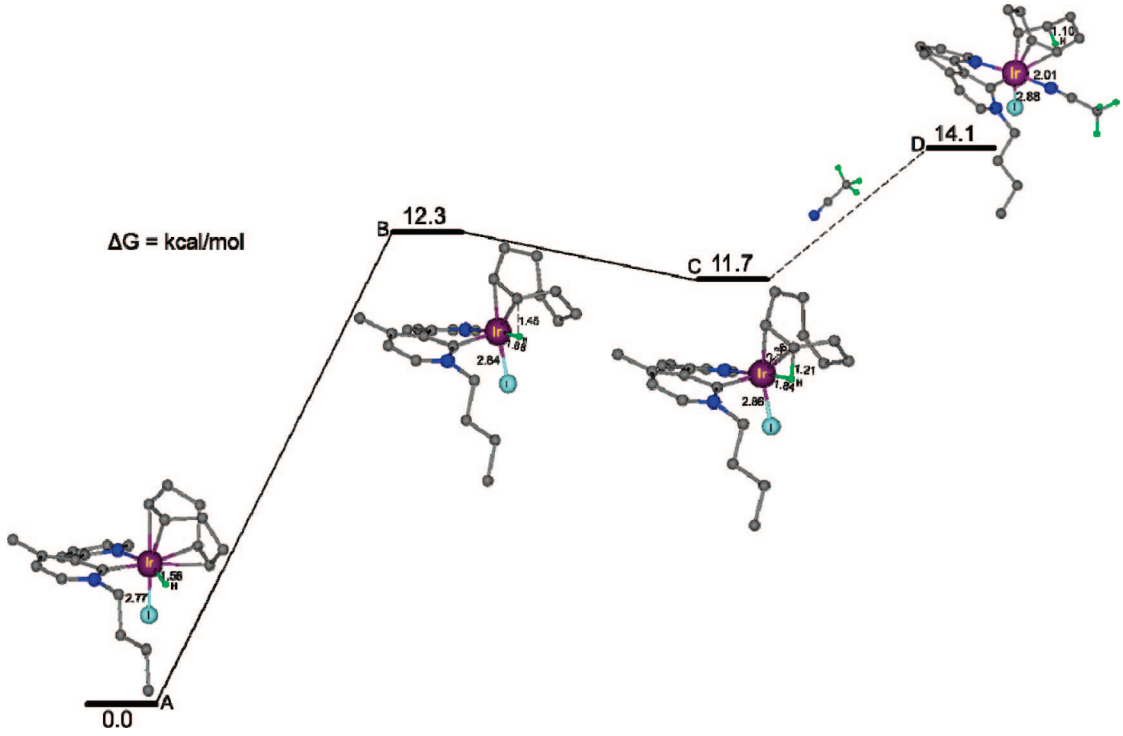


Figure 3. Energy profile of β-H insertion reaction of **5**.

insertion. However, no reaction took place when **5** was heated in CD_2Cl_2 in an sealed NMR tube (39 °C, 24 h). Prolonged heating of **5** in CD_3CN or in CH_2Cl_2 with 3 equiv of PPh_3 afforded unidentified products among which multiples hydride species were detected. Thus it follows that β-hydride insertion here can be thermodynamically unfavorable or has a high kinetic barrier. We then carried out computational studies to further understand this step. Calculations were performed at the DFT level by means of the BL3YP/6-31G*/LANL2DZ(Ir and I) as implemented in Gaussian 2003. The structures of the reactant (**A**), transition state (**B**), intermediate (**C**), and product (**D**) were fully optimized, and the effect of the dichloromethane solvent was evaluated using the continuum PCM model (Figure 3). The β-H insertion product turned out to be a C−H agostic intermediate with Ir···H (1.84 Å), Ir···C (2.36 Å), and C−H (1.21 Å) distances comparable to typical values reported for iridium agostic complexes. This insertion step has a pronounced late transition state with $\Delta G° = 11.7$ kcal/mol and $\Delta G^{\ddagger} = 12.3$ kcal/mol. Subsequent substitution of the C−H agostic bond in **C** by MeCN further carries slightly uphill thermodynamics ($\Delta G = 2.4$ kcal/mol), and overall product **D** is thermodynamically unfavorable by 14.1 kcal/mol. These theoretical data indicate that this step is indeed both thermodynamically and kinetically unfavorable.

Thermodynamics of *cis* and *trans* Isomers. We then further carried out theoretical studies to explore the energetics of the *N*-methyl analogue of complex **6a** and its possible *trans* isomer. The calculated structure of this *cis N*-methyl analogue isomer is comparable to that of **5** obtained from either experimental (X-ray crystallography) or computational methods (see Supporting Information). In the *cis* isomer, the olefinic C═C bonds are perpendicular to the plane defined by the carbene, iridium, and iodide, whereas they are parallel in the *trans* isomer (Figure 4). The calculated internal energies of these two isomers in the gas state indicate that the *trans* isomer is energetically unfavorable by 6.8 kcal/mol, which is consistent with the fact that only the *cis* isomer was observed in solution NMR spectroscopy.

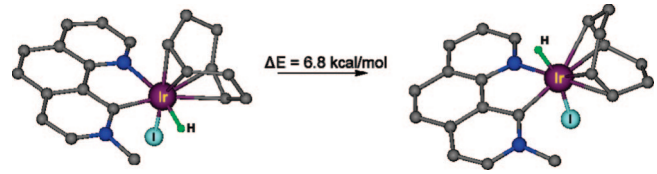
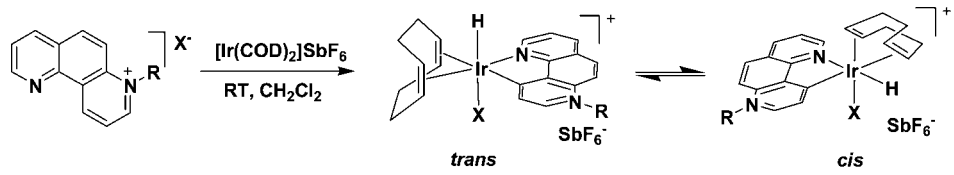


Figure 4. Comparison of two stereoisomeric iridium(III) py-NHC hydides.

Remote py-NHC Complexes. Encouraged by improved selectivity and the single isomer obtained for complexes **5** and **6a**,**b**, ligands **4a**−**c** were allowed to react with $[Ir(COD)_2]SbF_6$ (Scheme 1), where the products are remote py-NHC complexes. These products represent the first samples of iridium remote py-NHC complexes. In contrast to py-NHC complexes **5** and **6a,b**, each reaction yields an equilibrium mixture of two hydride complexes in solution (Scheme 1). For instance, in the ^{1}H NMR spectra (CD_2Cl_2) of iridium(III) iodide **7a** or **7c**, two hydride signals were observed (δ −14.13 and −12.81 for **7a** and −14.11 and −12.62 for **7c**), and the corresponding ratio is 10:1 in each case (Table 1). These two hydride complexes are assigned to two stereoisomeric products (*cis* and *trans* isomers). Pure **7a**-*cis* or **7c**-*cis* could be obtained as single crystals from the recrystallization of the isomeric mixtures using CH_2Cl_2 and Et_2O. Correlations between the solid structure and the ^{1}H NMR spectrum could be achieved by dissolution of a pure sample of **7a**-*cis* at −40 °C, followed by ^{1}H NMR analysis (Table 1). The *cis* hydride resonates at a higher field and is the major isomer for both **7a** and **7c** (Table 1 and Scheme 1). The remote py-NHC carbon atoms resonate at δ 191.1 (**7a**-*cis*) and 192.5 (**7c**-*cis*) in the ^{13}C NMR spectra, which are slightly deshielded compared with those in complexes **5** and **6a**,**b**. Halide effects have also been observed: the ratio of **7b**-*cis* to **7b**-*trans* decreases to 4.5:1 when bromide is used. One explanation of the higher *cis* to *trans* ratio observed for

Scheme 1. Synthesis of Iridium(III) Remote py-NHC Hydrides



4a R=^{n}Bu, X=I	**7a**	1	10
4b R=benzyl, X=Br	**7b**	1	4.5
4c R=benzyl, X=I	**7c**	1	10

iodide complexes is that the high *trans* effects of both the hydride and iodide will render the *trans* product unfavorable.

Equilibrium between the *cis* and *trans* Iridium Hydride Remote py-NHC Complexes. The equilibrium between **7a**-*cis* and **7a**-*trans* was further studied by NMR spectroscopy in CD_3CN. The van't Hoff plot of this *trans* to *cis* equilibrium system gave thermodynamic parameters $\Delta H° = 1.6$ kcal/mol and $\Delta S° = -0.77$ eu (see Supporting Information), and this reaction is nearly thermoneutral. The equilibrium between **7b**-*cis* and **7b**-*trans* is even less sensitive to temperature so that no thermodynamic parameters could be accurately measured.

X-ray Crystallographic Analyses. Single crystals of **5**, **6b**, and**7a** were analyzed by X-ray crystallography (Figures 5−7 and Tables 2 and 3). Each of these complexes adpots a *pseudo*-octahedral geometry. In sharp contrast to the *trans* orientation of hydride and halide in previously reported Ir(III) NHC hydride complexes obtained from C−H activation,[22,23] the hydrides here are consistently *cis* to the halides. In all cases, one of the C═C bonds in the COD is *trans* to the carbene, while the other C═C bond is *trans* to the halide. The C═C bonds of the COD ligand all adopt upright conformation with respect to the plane defined by the $C_{carbene}$, Ir, and the halide. The olefin unit *trans* to the carbene gives Ir−C_{olefin} distances ca. 0.05Å longer than that *trans* to the halide, suggestive of the high *trans* effect of the carbene ligand in each complex. The Ir−C(18) distance (2.006(3) Å) in remote py-NHC complex **7a** is slightly shorter than that in py-NHC complex **6b** (2.030(4) Å). The C(18)−Ir−N(1) angle (79.05(12)°) in remote py-NHC complex **7a** is comparable to the corresponding ones in complexes **5** [78.6(4)°] and **6b** [78.98(14)°]. The C(18)−C(19) bonds in py-NHC complexes **5** and **6b** are at least 0.04 Å longer than the other three C−C bonds in the same ring, a structural feature reported in other py-NHC complexes.[21,24]

Catalysis in Transfer Hydrogenation. Iridium bis(carbene) dihalide complexes have proven to be robust catalysts for ketone transfer hydrogenation, and Ir(III) monohydrides were also proposed as the active species.[25] We reason that hydride complexes **5**, **6**, and **7** could also be active catalysts in this reaction. Indeed, transfer hydrogenation between acetophenone and ^{i}PrOH proceeded smoothly in the presence of 10 mol % Cs_2CO_3 (eq 3 and Table 4) under reflux. Under these conditions, complexes **6a** (1 mol %) and **6b** (1 mol %)

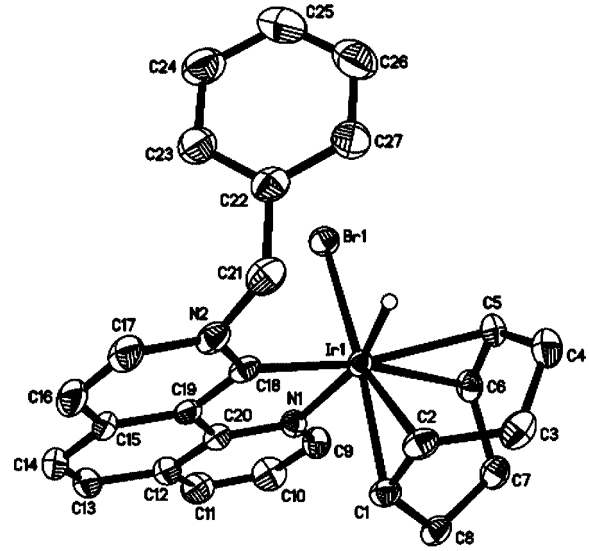


Figure 6. Molecular structure of **6b** (cation only) with ellipsoids shown at 50% thermal probability.

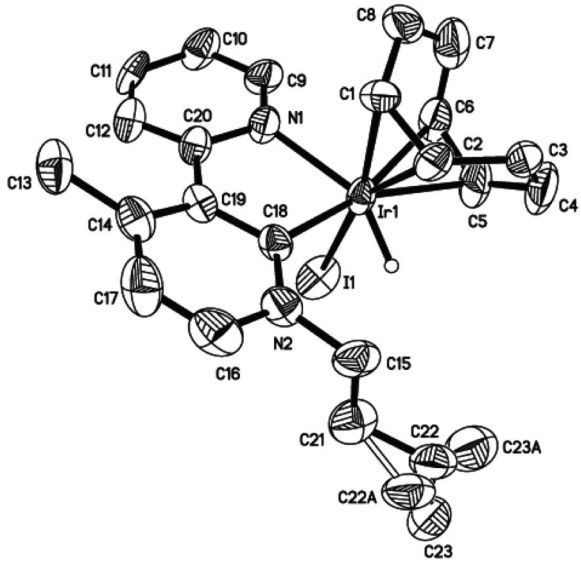


Figure 5. Molecular structure of **5** (cation only) with ellipsoids shown at 50% thermal probability.

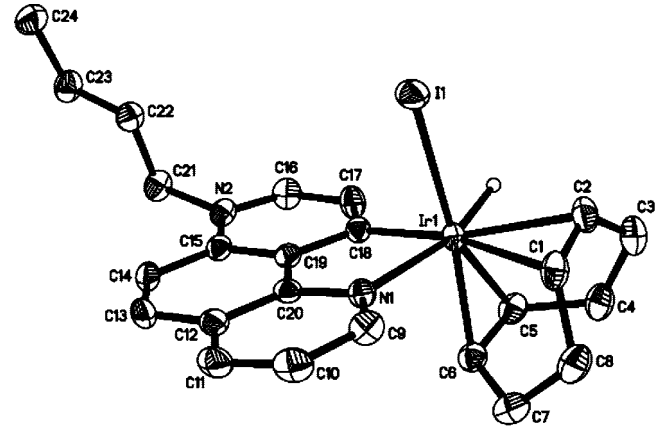


Figure 7. Molecular structure of **7a** (cation only) with ellipsoids shown at 50% thermal probability.

Table 2. Crystallographic Data for Complexes 5, 6b, and 7a

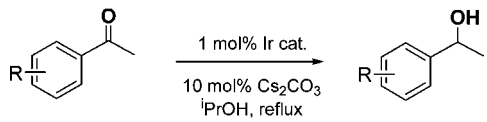
	5	6b · 1/3CH$_3$CN	7a
empirical formula	$C_{23}H_{31}F_6IrN_2P$	$C_{27}H_{27}BrF_6IrN_2Sb \cdot 1/3CH_3CN$	$C_{24}H_{29}F_6IrN_2Sb$
formula weight	799.57	901.05	900.34
temperature		173(2) K	
crystal system	monoclinic	triclinic	monoclinic
space group	*P*2(1)/*n*	*P*-1	*P*2(1)/*c*
a (Å)	11.3177(2)	13.0166(4)	14.5088(4)
b (Å)	12.8037(3)	13.5422(4)	12.9346(3)
c (Å)	17.9585(4)	24.0445(7)	14.1699(4)
α (deg)	90	85.1270(10)	90
β (deg)	91.1430(10)	82.9790(2)	99.8920(4)
γ (deg)	90	87.9560(10)	90
V (Å^3)	2601.82(10)	4190.0(2)	2619.67(12)
Z	4	6	4
d_{calcd} (g/cm^3)	2.041	2.143	2.283
μ (mm^{-1})	6.437	7.219	7.343
crystal size (mm)	0.30 × 0.26 × 0.16	0.30 × 0.12 × 0.10	0.30 × 0.18 × 0.06
total, unique no. of rflns	35948, 4612	176183, 41000	40906, 5716
R(int)	0.0334	0.0385	0.0237
data, restraints, parameters	4612, 196, 369	41000, 9, 1064	5716, 3, 320
R, R_w (all data)	0.0582, 0.1116	0.0848, 0.1210	0.0220, 0.0456
GOF	1.206	1.035	1.055
peak and hole (e Å^{-3})	3.278, −2.246	2.722, −2.987	2.619, −1.099

Table 3. Selected Bond Lengths and Angles for Complexes 5, 6b, and 7a

	5	6b	7a
Ir−C(18) (Å)	2.013(9)	2.030(4)	2.006(3)
Ir−N(1) (Å)	2.193(8)	2.204(3)	2.209(3)
Ir−X (Å)	2.7069(10)	2.5089(4)	2.6901(3)
C(18)−C(19) (Å)	1.426(14)	1.415(6)	1.415(4)
C(18)−Ir−N(1) (deg)	78.6(4)	78.98(14)	79.05(12)
C(18)−Ir−X (deg)	91.1(3)	91.53(10)	88.99(9)
N(1)−Ir−X (deg)	84.8(2)	84.61(8)	85.78(7)

exhibited essentially the same catalytic activity, giving 92% and 90% yields, respectively, after 6 h. A lower yield (74%) was obtained when the loading of **6a** was reduced to 0.1 mol % (entry 2). Other methyl aryl ketones could also be reduced to the corresponding alcohols in high NMR yields (82−99%). In general substrates with electron-withdrawing groups (entries 5−8) tend to show higher reactivity than those with electron-donating groups (entry 4).

The catalytic reaction was further extended to the transfer hydrogenation of α,*β*-unsaturated ketones and aldehydes, where chemoselectivity can be an issue.[26] The results are given in Table 4, and both C═C and C═O double bonds were hydrogenated for the substrates examined. Transfer hydrogenation of cinnamaldehyde afforded only 70% NMR yield (entry 15), although a nearly full conversion was achieved. It is apparently possible that transfer hydrogenation of enones could occur on the C═C bond first and then on the C═O group. To further test whether the other stepwise sequence is possible, we then examined an allylic alcohol *trans*-PhCH═CHC(OH)Me, which can be cleanly hydrogenated under the same reaction conditions (entry 13). These results suggest that transfer hydrogenation here can follow either stepwise sequence. In comparison, hydrogenation of α, *β*-unsaturated carbonyl compounds at the C═C bonds catalyzed by Cu[27] and Ru[28] have been reported and this chemoselectivity compliments the traditional hydride reduction protocols.



(3)

Electronic Effects of Pyridine-Based NHCs. The distinctive *σ*-donating characters of carbon-centered ligands are undoubtedly relevant to their increasingly important roles in homogeneous catalysis,[21] and major advances have been focused on the development of electron-rich ligands of late transition metal complexes. The IR stretching frequencies of CO groups in dicarbonyl rhodium complex RhCl(CO)$_2$L are commonly used to assess the electronic properties of a given ligand L. A more donating ligand should result in a lower CO stretching frequency. Synthesis of iridium CO complexes with py-NHC or remote py-NHC ligands met with failure. Thus the electronic effects of these py-NHC and remote py-NHC ligands were evaluated for their rhodium complexes and were compared with those of normal and abnormal NHC ligands by theoretical methods (Figure 8). The ν_{CO} frequencies of complexes **8**−**11** were calculated at the B3LYP/6-31G*/LANL2DZ (Rh) level (see Supporting Information), and the average ν_{CO} values are directly related to their donating ability. Py-NHC and remote py-NHC ligands are essentially the same in donating capacity (2149.3 cm^{-1} for both **8** and **9**). Either the normal or abnormal imidazole-based NHCs in **10** (2155.1 cm^{-1}) and **11** (2160 cm^{-1}) are slightly less donating than the py-NHC and the remote py-NHC. A general order of donating ability of py-NHC ≅ remote py-NHC > abnormal NHC > normal NHC can be concluded, consistent with previous reports.[13,21]

Conclusions

We have described a mild and straightforward synthetic procedure for py-NHC and remote py-NHC hydride complexes of iridium by means of nitrogen-assisted activation of C−H bonds in pyridine-tethered pyridiums. X-ray crystal structures of representative iridium py-NHC and remote py-NHC complexes were determined, and in all cases a mutual *cis* orientation of the halide and hydride ligands was observed in the solid state. For iridium(III) remote py-NHC hydries, both *cis* and *trans* (with respect to the hydride and the halide) isomers have been observed in the solution state and are in equilibration. No *β*-H insertion reaction was observed for these iridium(III) hydride complexes, and theoretical studies

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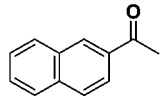
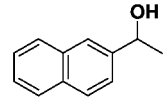
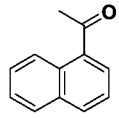
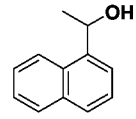
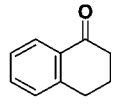
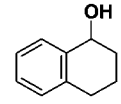
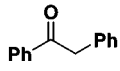
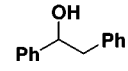
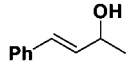
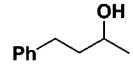
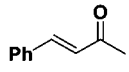
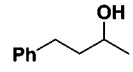
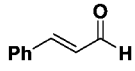
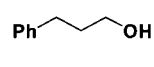
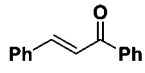
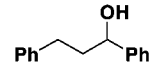
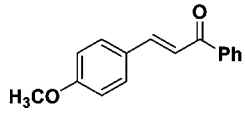
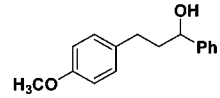
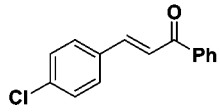
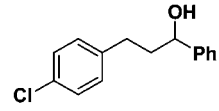
Table 4. Transfer Hydrogenation of Acetophenones and α,β-Unsaturated Ketones and Aldehydes[a]

entry	ketone	time (h)	products	yield (%)[b]
				
1	Ar = Ph	6		92, 90[c]
2	Ar = Ph	6		74[d]
3	Ar = 4-MeC_6H_4	4		93
4	Ar = 4-$MeOC_6H_4$	6		82
5	Ar = 4-BrC_6H_4	3		99
6	Ar = 4-FC_6H_4	3		99
7	Ar = 4-ClC_6H_4	4		95
8	Ar = 3-BrC_6H_4	4		99
9		6		95
10		4		99
11		8		82
12		13		86
13		6		95
14		10		88
15		10		70
16		4		96
17		10		92
18		6		96

[a] Reaction condition: 1 mmol of acetophenone; 0.1 mmol of Cs_2CO_3; 1 mol % of catalyst **6a**; 3 mL of ^{i}PrOH. [b] NMR yield using 1,3,5-trimethoxybenzene as an internal standard. [c] Compound **6b** (1 mol %) as the catalyst. [d] Compound **6b** (0.1 mol %) as the catalyst.

indicate that this step is thermodynamically unfavorable. These iridium py-NHC hydride complexes have shown high catalytic activities in ketone transfer hydrogenation. DFT calculations on $[Rh(CO)_2(N\wedge NHC)]^+$ complexes have revealed that py-NHCs and remote py-NHCs are more donating than normal and abnormal imidazole-based NHCs. Extension of the synthetic methodology of pyridine-based NHC complexes to other transition metals and widening of the scope of catalytic applications of these py-NHC complexes are currently under investigation in our laboratory.

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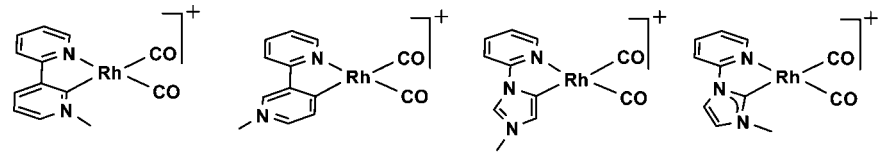

	8 py-NHC	**9** remote py-NHC	**10** abnormal NHC	**11** normal NHC
υ_{CO} (cm^{-1})	2124.8, 2173.8	2127.0, 2171.6	2134.5, 2175.7	2138.0, 2182.1
average (cm^{-1})	2149.3	2149.3	2155.1	2160

Figure 8. Calculated CO stretching frequencies of complexes **8**−**11**.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk techniques or in a nitrogen-filled dry box, except where otherwise noted. All solvents were distilled under N_2 before use and were stored in a dry box. $CDCl_3$ was dried by 4 Å molecular sieves. CD_2Cl_2, DMSO-d_6, and CD_3CN were obtained in sealed ampoules from CIL and were used without further purification. Air-sensitive compounds were stored and weighed in a dry box. NMR spectra were recorded on a Bruker 300 or 500 MHz or a JEOL 400 MHz spectrometer. All spectra were obtained at 298 K unless otherwise specified. Temperatures (>295 K) of NMR samples for thermodynamic studies were calibrated using 80% ethylene glycol in DMSO-d_6. The chemical shift is given as dimensionless δ values and is referenced relative to $SiMe_4$ for ^1H and ^{13}C NMR spectroscopy. Elemental analyses were performed in the Division of Chemistry and Biological Chemistry, Nanyang Technological University. HRMS spectra were obtained in ESI mode on a Waters Micromass Q-Tof Premier Mass Spectrometer.

Compound 1. 2,3′-Bipyridine (160 mg, 1.02 mmol) and 1-iodobutane (188 mg, 1.02 mmol) were dissolved in acetonitrile (5 mL), and the mixture was loaded into a sealed pressure tube and stirred at 120 °C for 24 h. The solvent was then removed under reduced pressure. The residue obtained was washed with diethyl ether to give a light yellow solid, which was used without further purification. Yield: 320 mg (0.94 mmol, 92%). ^1H (500 MHz, $CDCl_3$): δ 9.96 (s, 1H), 9.46 (d, J = 5.4 Hz, 1H), 9.26 (d, J = 8.0 Hz, 1H), 8.74 (d, J = 3.9 Hz, 1H), 8.52 (d, J = 8.0 Hz, 1H), 8.25 (t, J = 6.8 Hz, 1H), 7.97 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 6.8 Hz, 1H), 5.13 (t, J = 7.4 Hz, 2H, N−CH_2), 2.11 (t, J = 7.4 Hz, 2H, CH_2), 1.50 (q, J = 7.5 Hz, 2H, CH_2), 1.00 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C (100 Hz, $CDCl_3$): δ 150.4, 149.2, 144.3, 142.7, 142.4, 139.7, 138.2, 128.6, 125.4, 122.8, 62.2 (NCH_2), 34.0 (NCH_2CH_2), 19.4 ($NCH_2CH_2CH_2$), 13.7 (CH_3). HRMS (ESI^+): 213.1385, calcd mass for $[C_{14}H_{17}N_2]^+$ 213.1392.

Compound **2** was synthesized as a yellow powder in 91% yield by following a method directly analogous to that for **1** starting from 4-methyl-3-(pyridin-2-yl)pyridine and 1-iodobutane. ^1H (400 MHz, $CDCl_3$): δ 9.30 (d, J = 6.4 Hz, 1H), 9.12 (s, 1H), 8.70 (d, J = 5.0 Hz, 1H), 8.04 (d, J = 7.8 Hz, 1H), 7.99 (d, J = 6.4 Hz, 1H), 7.92 (td, ^3J = 7.8 Hz, ^2J = 1.8 Hz, 1H), 7.41−7.43 (m, 1H), 4.96 (t, J = 7.4 Hz, 2H, N−CH_2), 2.69 (s, 3H, CH_3), 2.19 (t, J = 7.8 Hz, 2H, CH_2), 1.42 (q, J = 7.8 Hz, 2H, CH_2), 0.92 (t, J = 7.3 Hz, 3H, CH_3). ^{13}C (100 MHz, $CDCl_3$): 157.7, 151.7, 150.0, 143.5, 143.0, 140.0, 137.9, 130.3, 125.6, 124.4, 61.4, 33.7, 21.6, 19.4, 13.7. HRMS (ESI^+): 227.1543, calcd mass for $[C_{15}H_{19}N_2]^+$ 227.1548.

Compound **3a** was synthesized as a white solid in 88% yield by following a method directly analogous to that for **1** starting from 1,9-phenanthroline and 1-iodobutane. ^1H (400 MHz, $CDCl_3$): δ 10.43 (s, 1H), 9.60 (d, J = 6.7 Hz, 1H), 9.12 (d, J = 3.7 Hz, 1H), 8.73 (d, J = 6.7 Hz, 1H), 8.47 (d, J = 8.0 Hz, 1H), 9.43 (d, J = 9.2 Hz, 1H), 8.20 (d, J = 9.2 Hz, 1H), 7.82 (dd, J = 4.3 Hz, 7.9 Hz, 1H), 5.15 (t, J = 7.9 Hz, 2H, N−CH_2), 2.17 (t, J = 7.3 Hz, 2H, CH_2), 1.49 (q, J = 7.4 Hz, 2H, CH_2), 0.97 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C (100 MHz, $CDCl_3$): δ 152.1, 144.2, 143.3, 140.8, 139.6, 137.9, 137.3, 127.8, 127.3, 126.9, 125.5, 124.9, 62.7, 34.0, 19.5, 13.7. HRMS (ESI^+): 237.1382, calcd mass for $[C_{16}H_{17}N_2]^+$ 237.1392.

Compound **3b** was synthesized as a white solid in 96% by following a method directly analogous to that for **1** starting from 1,9-phenanthroline and benzyl bromide. ^1H (400 MHz, DMSO-d_6): δ 10.90 (s, 1H), 9.20−9.23 (m, 2H), 8.74 (d, J = 6.4 Hz, 1H), 6.70 (d, J = 9.1 Hz, 1H), 8.62 (d, J = 9.1 Hz, 1H), 8.27 (d, J = 8.7 Hz, 1H), 7.96 (dd, J = 8.3, 4.6 Hz, 1H), 7.62 (d, J = 8.3 Hz, 2H), 7.40−7.43 (m, 3H), 6.19 (s, 2H). ^{13}C (100 MHz, DMSO-d_6): δ 152.5, 145.1, 144.5, 141.0, 139.4, 138.1, 135.2, 129.8, 129.7, 129.5, 128.0, 127.2, 126.9, 125.9, 125.4, 63.8 (CH_2). HRMS (ESI^+): 271.1229, calcd mass for $[C_{19}H_{15}N_2]^+$ 271.1235.

Compound **4a** was synthesized as a white solid in 85% yield by following a method directly analogous to that for **1** starting from 1,7-phenanthroline and 1-iodobutane. ^1H (400 MHz, $CDCl_3$): δ 10.27−10.32 (m, 2H), 9.18 (dd, J = 4.1, 1.4 Hz, 1H), 8.60 (dd, J = 9.6, 20.6 Hz, 2H), 8.51 (dd, J = 8.2, 1.4 Hz, 1H), 8.31 (dd, J = 8.2, 5.9 Hz, 1H), 7.83 (dd, J = 8.2, 4.5 Hz, 1H), 5.51 (tr, J = 7.3 Hz, 2H, N−CH_2), 2.11−2.15 (m, 2H, CH_2), 1.55−1.58 (m, 2H, CH_2), 0.96 (tr, J = 7.4 Hz, 3H, CH_3). ^{13}C (100 MHz, $CDCl_3$): δ 152.5, 149.1, 144.2, 142.7, 139.9, 137.5, 137.0, 130.0, 126.4, 125.2, 123.4, 116.8, 59.0, 32.7, 19.9, 13.8. HRMS (ESI^+): 237.1388, calcd mass for $[C_{16}H_{17}N_2]^+$ 237.1392.

Compound **4b** was synthesized as a white solid in 95% yield by following a method directly analogous to that for **1** starting from 1,7-phenanthroline and benzyl bromide. ^1H (400 MHz, DMSO-d_6): δ 10.35 (d, J = 8.2 Hz, 1H), 9.90 (d, J = 6.0 Hz, 1H), 9.30 (dd, J = 4.1, 1.4 Hz, 1H), 8.72−8.76 (m, 2H), 8.53−8.58 (m, 2H), 8.01 (dd, J = 8.2, 4.6 Hz, 1H), 7.35−7.42 (m, 5H), 6.55 (s, 2H, NCH_2).. ^{13}C (100 MHz, DMSO-d_6): δ 153.1, 150.1, 143.8, 143.3, 140.6, 137.9, 137.2, 134.6, 129.9, 129.6, 129.3, 127.8, 126.5, 125.8, 124.5, 117.8, 60.8 (CH_2). HRMS (ESI^+): 271.1230, calcd mass for $[C_{19}H_{15}N_2]^+$: 271.1235. Anal. Calcd for **4b** ($C_{19}H_{15}BrN_2$): C, 64.97; H, 4.30; N, 7.98. Found: C, 65.11; H, 4.19; N, 8.08.

Synthesis of 4c. An excess of KI (900 mg, 5.42 mmol) was added to a solution of **4b** (300 mg, 0.86 mmol) in methanol (10 mL), and the mixture was stirred at room temperature for 12 h. The solvent was then removed under reduced pressure, and to this residue was added dichloromethane (15 mL). A clear solution was obtained after filtration. Removal of the solvent followed by addition of diethyl ether gave **1b** as a yellow solid in 81% yield (280 mg, 0.70 mmol). ^1H (400 MHz, DMSO-d_6): δ 10.35 (d, J = 8.2 Hz, 1H), 9.92 (d, J = 5.0 Hz, 1H), 9.30 (dd, J = 4.6, 1.8 Hz, 1H), 8.72−8.76 (m, 2H), 8.54−8.57 (m, 2H), 8.00 (dd, J = 8.2, 4.6 Hz, 1H), 7.40−7.42 (m, 5H). ^{13}C (100 MHz, DMSO-d_6): δ 153.1, 150.2, 143.8, 143.3, 140.7, 138.0, 137.3, 134.76, 130.0, 129.7, 129.3, 127.8, 126.5, 125.8, 124.5, 117.8, 60.8 (CH_2). HRMS (ESI^+): 271.1226, calcd mass for $[C_{19}H_{15}N_2]^+$: 271.1235. Anal. Calcd for

(28) (a) Ohta, T.; Takaya, H.; Kitamura, M.; Nagai, K.; Noyori, R. *J. Org. Chem.* **1987**, *52*, 3176. (b) Noyori, R.; Umeda, I.; Ishigami, T. *J. Org. Chem.* **1972**, *37*, 1542.

4c ($C_{19}H_{15}IN_2$) C, 57.30; H, 3.80; N, 7.03. Found: C, 57.39; H, 3.70; N, 7.11.

General Procedure for the Synthesis Iridium(III) py-NHC Hydride Complexes. To a stirred solution of $[Ir(COD)_2]PF_6$ or $[Ir(COD)_2]SbF_6$ (0.20 mmol) in CH_2Cl_2 (2 mL) was added a CH_2Cl_2 solution (3 mL) of a pyridinium salt (0.20 mmol). The mixture was stirred for 12 h at room temperature, after which time the red solution became light yellow or nearly colorless. The solution was then concentrated to ca. 0.5 mL followed by addition of diethyl ether (8 mL). A pale yellow or off-white precipitate appeared and was filtered and dried. Analytically pure iridium hydrides were obtained after recrystallization using CH_2Cl_2 and Et_2O.

Complex 5. Yield: 65%. Single crystals of **5** suitable for X-ray analysis were obtained by the slow diffusion of diethyl ether into its CH_2Cl_2 solution after 1 day. ^{1}H (300 MHz, CD_2Cl_2): δ 9.48 (d, J = 5.8 Hz, 1H), 9.48 (d, J = 6.5 Hz, 1H), 8.23 (d, J = 3.8 Hz, 2H), 7.71−7.76 (m, 1H), 7.36 (d, J = 6.5 Hz, 1H), 5.75 (apparent t, J = 7.8 Hz, 1H, COD), 5.31−5.38 (m, 1H, N−CH_2), 4.86−4.96 (m, 1H, COD), 4.69−4.76 (m, 1H, N−CH_2), 4.04−4.11 (m, 1H, COD), 3.28−3.33 (m, 1H, COD), 2.96−3.00 (m, 1H, COD), 2.89 (s, 3H, CH_3), 2.53−2.84 (m, 3H, COD), 2.40−2.45 (m, 1H, COD), 2.17−2.25 (m, 2H, CH_2), 1.78−2.10 (m, 3H, COD), 1.57−1.69 (m, 2H, CH_2), 1.14 (t, J = 7.4 Hz, 3H, CH_2CH_3), −13.52 (s, 1H, Ir-*H*). ^{13}C (75 MHz, $CDCl_3$): δ 182.5 (Ir-*C*), 160.8, 153.1, 149.1, 146.1, 141.5, 139.5, 126.5, 126.3, 126.2, 102.9 (*C*H of COD), 93.2 (*C*H of COD), 83.7 (*C*H of COD), 76.4 (*C*H of COD), 69.1 (N-*C*H_2), 36.2, 33.0, 32.6, 31.5, 25.3, 24.1 (*C*H_3), 19.9, 15.1, 13.4. Anal. Calcd for $C_{23}H_{31}F_6IIrN_2P$ (799.6): C, 34.35; H, 3.91; N, 3.50. Found: C, 34.29; H, 3.81; N, 3.44.

Complex 6a. Yield: 91%. ^{1}H (300 MHz, CD_2Cl_2): δ 9.72 (d, J = 5.6 Hz, 1H), 8.81 (dd, J = 8.2, 1.1 Hz, 1H), 8.53 (d, J = 6.9 Hz, 1H), 8.39 (d, J = 8.7 Hz, 1H), 8.09−8.16 (m, 2H), 7.91 (d, J = 6.8 Hz, 1H), 5.94 (apparent t, J = 8.0 Hz, 1H, COD), 5.37−5.46 (m, 1H, N−CH_2), 4.84−5.01 (m, 2H, 1H for N−CH_2 and 1H for COD), 4.46−4.53 (m, 1H, COD), 3.23−3.27 (m, 1H, COD), 3.09−3.16 (m, 1H, COD), 2.80−2.93 (m, 1H, COD), 2.55−2.73 (m, 3H, COD), 2.19−2.31 (m, 2H, CH_2), 1.94−2.08 (m, 2H, COD), 1.81−1.93 (m, 1H, COD), 1.62−1.70 (m, 2H, CH_2), 1.24 (t, J = 7.4 Hz, 3H, CH_2CH_3), −13.8 (s, 1H, Ir-*H*). ^{13}C (75 MHz, $CDCl_3$): δ 186.8 (Ir-*C*), 153.9, 153.3, 139.9, 139.7, 138.7, 138.8, 134.2, 129.6, 127.4, 125.7, 120.3, 103.0 (*C*H of COD), 93.0 (*C*H of COD), 82.4 (*C*H of COD), 76.6 (*C*H of COD), 69.8 (N-*C*H_2), 36.8, 33.2, 33.1 31.0, 25.1, 25.0, 11.1 (*C*H_3). Anal. Calcd for $C_{24}H_{29}F_6IIrN_2P$ (809.6): C, 35.61; H, 3.61; N, 3.46. Found: C, 35.79; H, 3.50; N, 3.82.

Complex 6b. Yield: 96%. Single crystals suitable for X-ray analysis were obtained by layering its CH_3CN/Et_2O solution with *n*-pentane after 1 day at room temperature. ^{1}H (400 MHz, CD_2Cl_2): δ 9.68 (d, J = 6.6 Hz, 1H), 8.82 (d, J = 7.6 Hz, 1H), 8.47 (d, J = 6.1 Hz, 1H), 8.42 (d, J = 9.2 Hz, 1H), 8.15−8.18 (m, 1H), 8.09 (d, J = 7.6 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.55−7.57 (m, 2H), 7.47−7.50 (m, 3H), 6.85 (d, J = 13.8 Hz, 1H, N−CH_2Ph), 6.31 (d, J = 13.8 Hz, 1H, N−CH_2Ph), 5.82 (apparent t, J = 9.2 Hz, 1H, COD), 5.82 (apparent q, J = 4.8 Hz, 1H, COD), 4.07 (apparent q, J = 4.6 Hz, 1H, COD), 3.14 (apparent t, J = 6.1 Hz, 1H, COD), 3.00−3.05 (m, 1H, COD), 2.80−2.88 (m, 1H, COD), 2.66−2.74 (m, 1H, COD), 2.29−2.40 (m, 2H, COD), 1.85−2.02 (m, 2H, COD), 1.67−1.78 (m, 1H, COD), −13.0 (s, 1H, Ir-*H*). ^{13}C (100 MHz, $CDCl_3$): δ 189.7 (Ir-*C*), 154.2, 153.3, 140.4, 140.3, 139.3, 137.2, 135.2, 135.1, 130.0, 129.7, 128.8, 127.8, 126.3, 121.0, 105.6 (*C*H of COD), 94.2 (*C*H of COD), 80.0 (*C*H of COD), 75.6 (*C*H of COD), 70.9 (N−CH_2Ph), 36.2 (*C*H_2 of COD), 33.8 (*C*H_2 of COD), 31.4 (*C*H_2 of COD), 24.8 (*C*H_2 of COD). Anal. Calcd for $C_{27}H_{27}BrF_6IrN_2Sb$ (887.4): C, 36.54; H, 3.07; N, 3.16. Found: C, 36.39; H, 3.01; N, 3.25.

Complexes 7a. Yield 82%. Single crystals of **7a**-*cis* suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into its acetone solution. ^{1}H (300 MHz, CD_2Cl_2) for **7a**-*cis*: δ 9.70 (d, J = 5.3 Hz, 1H), 8.81 (dd, J = 8.1, 1.0 Hz, 1H), 8.54 (d, J = 9.4 Hz, 1H), 8.42 (d, J = 6.2 Hz, 1H), 8.11−8.19 (m, 3H), 5.82 (apparent t, J = 7.8 Hz, 1H, COD), 4.85−4.94 (m, 1H, COD), 4.69−4.82 (m, 2H, N−CH_2), 4.45−4.52 (m, 1H, COD), 3.01−3.09 (m, 1H, COD), 2.88−2.94 (m, 1H, COD), 2.77−2.85 (m, 1H, COD), 2.60−2.74 (m, 1H, COD), 2.24−2.29 (m, 1H, COD), 1.91−2.12 (m, 6H, 2H for CH_2 and 4H for COD), 1.47−1.59 (m, 2H, CH_2), 1.04 (t, J = 7.3 Hz, 3H, CH_2CH_3), −14.1 (s, 1H, Ir-*H*). ^{13}C NMR (100 MHz, CD_2Cl_2) for **7a**-*cis*: δ 191.1 (Ir-*C*), 154.3, 153.4, 141.6, 140.2, 139.3, 137.2, 135.2, 135.0, 127.9, 125.9, 118.2, 102.6 (*C*H of COD), 93.5 (*C*H of COD), 78.0 (*C*H of COD), 75.7 (*C*H of COD), 54.0 (N-*C*H_2), 36.2, 33.6, 32.1 31.2, 25.0, 19.9, 12.2 (*C*H_3). Anal. Calcd for $C_{24}H_{29}F_6IIrN_2Sb$ (900.4): C, 32.02; H, 3.25; N, 3.11. Found: C, 32.22; H, 3.29; N, 3.21.

Observation of the Equilibrium Mixture of Complexes 7b-*cis* and 7b-*trans*. **7b**-*cis* and**7b**-*trans* were obtained in 4.5:1 ratio in a CD_2Cl_2 solution. Yield: 91%. Selected NMR signals: ^{1}H NMR (400 MHz, CD_2Cl_2): −13.61 (Ir-*H*, **7b**-*cis*), −14.01 (Ir-*H,* **7b**-*trans*.). ^{13}C NMR (100 MHz CD_2Cl_2): 192.1 (Ir-*C,* **7b**-*cis*), 191.9 (Ir-*C,* **7b**-*trans*). Anal. Calcd for $C_{27}H_{27}F_6BrIrN_2Sb$ (887.4) C, 36.54; H, 3.07; N, 3.16; Found C, 36.31; H, 3.12; N, 3.07.

Complex 7c. Yield: 85%. ^{1}H (400 MHz, CD_2Cl_2) for **7c-*cis***: δ 9.70 (d, J = 6.1 Hz, 1H), 8.79 (d, J = 7.6 Hz, 1H), 8.47 (d, J = 6.1 Hz, 1H), 8.42 (d, J = 9.2 Hz, 1H), 8.20 (d, J = 6.1 Hz, 1H), 8.17 (d, J = 9.2 Hz, 1H), 8.10−8.14 (m, 1H), 7.43−7.48 (m, 3H), 7.26−7.28 (m, 2H), 5.95 (q, J = 15.8 Hz, 2H, N−CH_2), 5.83 (apparent t, J = 7.6 Hz, 1H, COD), 4.89−4.94 (m, 1H, COD), 4.50−4.53 (m, 1H, COD), 3.01−3.10 (m, 1H, COD), 2.96−2.99 (m, 1H, COD), 2.77−2.86 (m, 2H, COD), 2.58−2.70 (m, 2H, COD), 2.25−2.30 (m, 1H, COD), 1.98−2.04 (m, 2H, COD), −14.11 (s, 1H, Ir-*H*). ^{13}C NMR (100 MHz, CD_2Cl_2) for **7a-*cis***: δ 192.4 (Ir-*C*), 154.3, 153.3, 141.6, 140.3, 139.3, 137.6, 135.2, 135.0, 132.2, 129.8, 129.7, 128.0, 127.4, 125.9, 118.6, 102.7 (*C*H of COD), 93.6 (*C*H of COD), 78.2 (*C*H of COD), 75.9 (*C*H of COD), 59.9 (N-*C*H_2), 36.2 (*C*H_2 of COD), 33.5 (*C*H_2 of COD), 31.2 (*C*H_2 of COD), 25.0 (*C*H_2 of COD). Anal. Calcd for $C_{27}H_{27}F_6IIrN_2Sb$ (934.4): C, 34.71; H, 2.91; N, 3.00. Found: C, 34.65; H, 3.06; N, 3.11.

General Procedure for Iridium-Catalyzed Transfer Hydrogenation Reactions. An oven-dried flask was charged with acetophenone (1.0 mmol), Cs_2CO_3 (0.10 mmol), and internal standard 1,3,5-tri-*tert*-butylbenzene (0.30 mmol). ^{i}PrOH (3 mL) was then added, and the mixture was degassed by bubbling N_2 through the solution. An iridium catalyst (1 mol %) was added under a steady flow N_2. The mixture was refluxed for a time specified in Table 4. The volatiles were then removed under vacuum. The yields given in Table 4 are based on ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. The identity of the products of entries 15−17 (Table 4) were confirmed by comparisons with reported NMR data.[26a]

X-ray Crystallography. X-ray-quality single crystals of **5** were obtained by the slow diffusion of diethyl ether into its CH_2Cl_2 solution after 1 day. Single crystals of **6b** suitable for X-ray crystallographic analysis were obtained by layering its CH_3CN and Et_2O solution with *n*-pentane at room temperature. Single crystals of **7a**-*cis* suitable for X-ray analysis were obtained by the slow diffusion of diethyl ether into its acetone solution. Three molecules of **6b** cocrystallize with one part of MeCN, and these three molecules are slightly different in corresponding bond lengths and angles, so only one of them has been discussed. Crystal data were collected on a Bruker X8 Kappa CCD diffractometer at 173 K using graphite-monochromated Mo Kα radiation (λ = 0.71063 Å). The APEX2 software suite (Bruker 2005) was used for data acquisition, structure solution, and refinement. Absorption corrections were

applied using SAD-ABS. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using Xshell.

Computational Methods. All calculations were performed using the Gaussian 2003 program. DFT calculations were carried out using three-parameter hybrid function of Becke with the Lee−Yang−Parr correlation functional theory (B3LYP). The standard basis set 6-31G* was used for C, H, N, and O atoms, while the Lanl2dz ECP basis set was adopted for Rh and I atoms. Geometry optimizations were carried out without any geometrical constraints. All geometries were subjected to frequency analysis and characterized as a minimum (no imaginary frequencies).

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Supporting Information Available: Text, figures, and tables giving crystal data of **5**, **6b**, and **7a**; measurements of the equilibrium mixture of **7a** by VT NMR; atom coordinates of calculated structures; and NMR spectra of all the iridium hydride products. This material is available free of charge via the Internet at http://pubs.acs.org.

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