Transfer Hydrogenation of Imines and Alkenes and Direct Reductive Amination of Aldehydes Catalyzed by Triazole-Derived Iridium(I) Carbene Complexes

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A series of new iridium(I) triazole-based NHC complexes [(cod)Ir(NHC)L]BF_4 (L = PPh_3, pyridine) were prepared and showed good activity for transfer hydrogenation on C═O, C═N, and C═C double bonds in 2-propanol with K_2CO_3. The phosphine series was shown to be more active than the pyridine series in the case of imine transfer hydrogenation. A neopentyl wingtip substituent on the NHC gave the best catalytic activity with the following competitive order: aldehyde > ketone > imine. In a substrate containing both aldehyde and ketone functionalities, only the aldehyde was reduced. Of great interest, the transfer hydrogenation of polarized and nonpolarized C═C bonds was also proved possible. In a useful organic synthetic application, direct, one-pot reductive amination of RCHO with $R'NH_2$ to give RCH_2NHR' was shown for a variety of cases.

Introduction

N-heterocyclic carbenes (NHCs) have sometimes been considered alternatives to phosphines as spectator ligands in homogeneous catalysis and share with them the possibility of tuning catalyst activity by varying the substitution scheme of the ligand.[1−7] Steric tuning of NHCs is possible by changing the R_1 and R_2 substituents at nitrogen, while electronic properties are mainly governed by the nature of the azole ring. The recent work of Hermann et al. focuses on changing the azole and comparing the σ-donor ability of several NHC ligands.[8] Triazole-based NHCs (X = N; Figure 1) appear to have an electron donor power that lies between that of the conventional imidazole-2-ylidene (X = CH) NHCs and typical phosphines. 1,2,4-Triazolium salts with various substitution patterns are very accessible through the easy functionalization of *N*-alkyltriazole with alkyl bromide (Scheme 1). Triazolylidene ligands, relatively little studied so far, are thus very promising for catalytic applications. We decided to try triazolylidene complexes of Ir(I) for transfer hydrogenation of C═C, C═N, and C═O bonds, where they prove to be very active.

Transfer hydrogenation of unsaturated bonds is a reaction of great interest. On C═O double bonds, it has been extensively studied, leading to important applications such as racemization[9] of chiral alcohols and asymmetric reduction.[10] The synthetic power of this method has been extended to the production of amines, a family of molecules of great current interest, especially in biochemistry and the pharmaceutical industry.[11] Synthesis of amines can be achieved by reduction of a previously synthesized imine or by a one-pot reductive procedure (reductive amination) directly from an aldehyde and an amine. In the latter case a common method is to use sodium cyanoborohydride as a stoichiometric reductant, because it is selective for imine reduction.[12] However, catalytic reduction is preferred for large-scale industrial use in the hope of developing a greener chemistry by reducing waste production and energy use and lowering toxicity.[13] Excellent examples of catalytic imine hydrogenation, particularly the asymmetric variant using H_2 as

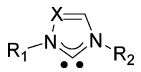
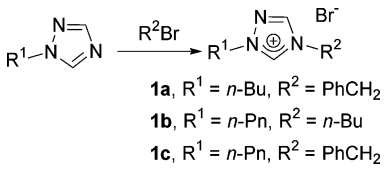


Figure 1. General structure of ligands used in this work (X = CH, N).

Scheme 1. Synthesis of Triazolium Salts 1a−c



1a, R^1 = *n*-Bu, R^2 = $PhCH_2$
1b, R^1 = *n*-Pn, R^2 = *n*-Bu
1c, R^1 = *n*-Pn, R^2 = $PhCH_2$

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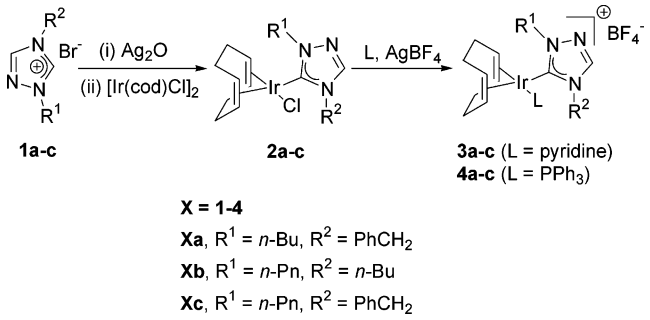
reductant, have been published recently.[14] However, hydrogen gas poses significant safety hazards, especially for large-scale industrial use; therefore, 2-propanol as a solvent and hydrogen donor is frequently seen. 2-Propanol is easy to use, inexpensive, and environmentally more benign. The volatile coproduct acetone can also be easily removed to shift any unfavorable equilibrium.[15] In related work, Noyori et al. have used formic acid/triethylamine azeotrope to reduce imines under mild conditions with high enantiomeric excess.[15] Transfer hydrogenation is more difficult for imines than for aldehydes and ketones, and few examples are known,[16−30] some being asymmetric.[17,31−33] Indeed, in this process, imine nitrogen lone pair coordination to the metal center is believed to inhibit isomerization to the π-bound form that is presumably needed for catalysis. NHC complexes of iridium and rhodium have shown useful activity: for instance, a variety of chelating rhodium and iridium bis(carbenes) have recently been shown to be very active in the transfer hydrogenation of aldehydes, ketones, and imines.[14] However, in comparison to ketone and imine transfer hydrogenation and olefin direct hydrogenation, olefin transfer hydrogenation has not previously been extensively studied. Very active catalysts for transfer hydrogenation have nevertheless failed for the challenging C=C case, where it is usually held that the lower polarity of the C=C bond is responsible for the failure.[34] Some examples are known,[35] but yields are usually low.[23,36]

We now extend this work by developing a series of new iridium(I) triazole-based NHC complexes. These compounds are obtained in high yields by simple methods in the presence of air. They show good activity for catalysis of transfer hydrogenation of imines with the mild base K_2CO_3 rather than the harsher KOH more usually encountered. Direct reductive amination of aldehyde and amine also proved possible.

Scheme 2. Synthesis of Iridium Complexes *X*a−c (*X* = 2−4)



Results and Discussion

The 1,2,4-triazolium salts **1a**−**c** were prepared by treating the appropriate 1-alkyltriazoles with neopentyl (*n*-Pn), *n*-butyl (*n*-Bu), or benzyl bromide in toluene at reflux for 16 h followed by isolation with diethyl ether (Scheme 1). The choice of N substituent groups in **1a**−**c** was dictated by two concerns: *n*-Bu, *n*-Pn, and benzyl were preferred to shorter chain alkyls for solubility reasons. *n*-Pn and benzyl avoid the potentially deleterious β-proton abstraction by the base. This, however, was not a problem, as both catalysts were stable in this respect. The triazolium salts **1a**−**c** have characteristic resonances in the ^{1}H NMR near 8.9 (C_3−H triazole proton) and 11.8 ppm (C_5−H triazole proton).

The metal complexes **2a**−**c** were prepared by in situ transmetalation from silver carbene complexes of compounds **1a**−**c** (Scheme 2).[37,38] Treatment with Ag_2O in CH_2Cl_2 at room temperature forms the intermediate silver carbene, which is poured directly into $[Ir(cod)Cl]_2$ in CH_2Cl_2. The mixture is stirred for 1 $^1/_2$ h, followed by filtration through Celite and removal of solvent to yield the yellow solids **2a**−**c**, which can be recrystallized from CH_2Cl_2/pentane to give [(cod)Ir(NHC)Cl] in good yield. All of the isolated complexes lack the C_5−H triazole proton resonance and show a signal for the C_3−H triazole proton in the range 7.70−7.87 ppm; thus, the "normal" CH carbene is formed. The product was fully characterized by NMR techniques and elemental analysis.

The pyridine-substituted iridium catalysts **3a**,**b** were made by treating **2a**,**b** with 1 equiv of pyridine and $AgBF_4$ in CH_2Cl_2 at room temperature under argon. Attempts to synthesize **3c** were frustrated by product instability. The triphenylphosphine analogues **4a**−**c** were all synthesized in the same way using PPh_3 instead of pyridine. The isolated complexes **3a**,**b** and **4a**−**c** were air stable both as solids and in solution. As before, the NMR evidence shows that the normal carbene is formed. Full characterization is included in the Experimental Section.

Attempts to make the tricyclohexylphosphine analogues were unsuccessful. Examination of models suggests an unacceptable steric clash between the bulky PCy_3 group and the azole ring.

Catalytic Reduction of Compounds Containing C=N and C=O. Prior work has shown that chelating imidazole- and triazole-derived NHC complexes of rhodium and iridium are excellent catalysts for hydrogen transfer.[14] Nolan et al.[39] have

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Table 1. Catalytic Transfer Hydrogenation of PhCH═NPh by 3 and 4[a]

	cat.				
	3a	**3b**	**4a**	**4b**	**4c**
yield[b] (%)	80	77	92	100	87

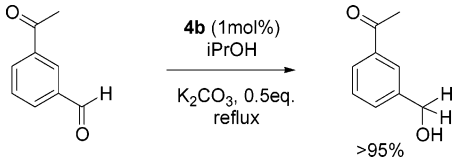
[a] Conditions: time, 30 min; 1% catalyst loading; *i*-PrOH, 10 mL; K_2CO_3, 0.5 mmol. [b]Based on substrate and numerically equivalent to catalytic turnovers.

Table 2. Reductive Amination by 4b[a]

		time (h)[b]		
R′	R	step 1	step 2	yield (%)
phenyl	phenyl	1	0.5	100
benzyl	phenyl	2	24	80[c]
phenyl	benzyl	3	24	73[c]
benzyl	benzyl	4	24	66[c]
n-hexyl	phenyl	2	24	73
isopropyl	phenyl	2	24	76

[a] Conditions: loading, 1.0% **4b**; K_2CO_3, 0.5 equiv. [b] Step 1, at 20 °C; step 2, at reflux with catalyst. [c] With cyclopentanol as solvent.

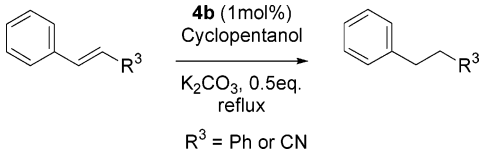
Scheme 3. Selective Hydrogenation on the Bifunctional Substrate 3-Acetylbenzaldehyde



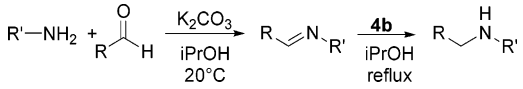
also shown transfer hydrogenation activity with monodentate imidazole-derived NHC complexes of iridium. We find catalysts **3a**,**b** and **4a**−**c** are also active for the transfer hydrogenation of imines. Comparison of the catalysts for activity in the transfer hydrogenation of the common substrate *N*-benzylideneaniline (Table 1) shows that **4b** is the most active, with 100% conversion in 30 min. The same reaction was tested with a catalyst charge of 0.6% with **4b**. Conversion was complete after 30 min, corresponding to a TOF of 333 h^{-1}. This system is thus one of the most active known for imine transfer hydrogenation, and comparable with that for the bidentate rhodium bis(imidazole) carbene complex (TOF = 100 h^{-1}, T = 85 °C) studied by our group previously,[20] with that for a pincer ruthenium bis(carbene) complex (TOF = 210 h^{-1}, T = 55 °C),[21] and with that for the ruthenium Cp derivatives of Bäckvall et al. (TOF = 213 h^{-1}, T = 70 °C, on 2-methylbenzylidenaniline).[22]

In a comparison of benzaldehyde, acetophenone, and *N*-benzylideneaniline pairwise as substrates, catalyst **4b** proved to have the expected competitive reactivity order: aldehyde > ketone > imine. The aldehyde was completely converted to the alcohol within 20 min before the imine was significantly hydrogenated (<5%) and the ketone was fully hydrogenated within 30 min, again before the imine was significantly hydrogenated (<5%). In contrast, Casey et al. found a Ru catalyst that was more active for imine than for ketone.[34] On the basis of these results, we decided to test a substrate that contains both an aldehyde and a ketone functionality within the same molecule, namely 3-acetylbenzaldehyde (Scheme 3). As hoped, on the basis of the competition studies, the aldehyde was indeed completely hydrogenated within 20 min, while the ketone group remained untouched. The fact that a ketone alone is readily reduced in 30 min, whereas the carbonyl group in the bifunctional compounds remain untouched after 20 min, is rationalized by the high selectivity of the catalyst, implying that the pathways have substantially different activation energies. This demonstrates that the catalyst is useful for the selective reduction of aldehydes over ketones, a relatively hard selectivity pattern to achieve by conventional means.[12]

Scheme 4. Transfer Hydrogenation on Stilbene and 3-Phenylacrylonitrile



Scheme 5. Reductive Amination



Alkene Transfer Hydrogenation. We then tested our best catalysts of transfer hydrogenation toward alkenes.[35] We were interested in determining if our catalytic system was active in this much harder reaction. Substrates with a polar and a nonpolar C═C bond were chosen: PhCH═CHCN and PhCH═CHPh (Scheme 4). Catalyst **4b** in 1 mol % gave 100% conversion to $PhCH_2CH_2CN$ and 75% conversion to $PhCH_2CH_2Ph$ after 16 h in refluxing cyclopentanol (bp 140 °C), which was used in place of *i*-PrOH to obtain a higher reaction temperature for these more difficult substrates. Reduction of both C═C bonds by transfer hydrogenation was possible, but as expected, the more polar C═C bond of PhCH═CHCN was reduced more quickly. These results compare with those of Williams et al., who showed [Cp*Ir]/dppp gives complete conversion of benzylcinnamate over 72 h at 150 °C.[35] Reduction of a symmetrical alkene such as this is rare.

Reductive Amination. The goal of this project was to pursue the direct, one-pot reductive amination of aldehydes. However, the selectivity pattern of the catalyst (C═O > C═N) requires that the imine must be formed prior to the addition of catalyst; otherwise, the aldehyde will be reduced (Scheme 5). In the first stage of our procedure (step 1), the imine is formed in situ by stirring 1 equiv of amine with the aldehyde in 2-propanol with K_2CO_3, which acts as a drying agent. Catalyst **4b** was then added (step 2) and gave complete conversion of the imine (R, R′ = Ph) to the amine with 1.0% loading in 30 min under reflux. Complete conversion was even observed with as low as 0.6% loading. No counterion effects[40,41] were noted in the series from BF_4^- to PF_6^- to SbF_6^-.

A variety of aldehydes and amines (Table 2) were tested for this reductive amination procedure, and the reaction is indeed successful for a wide range of partners, although a much longer reaction time was required for many of the substrates.

Conclusions

We have shown that these iridium(I) triazolium NHC catalysts are highly active for the transfer hydrogenation of imines as well as C═O and C═C groups. The activity observed in the difficult alkene transfer hydrogenation is of a particular interest. Direct, one-pot reductive amination of an amine and aldehyde also proved possible. The phosphine catalysts are found to be

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much more active than the pyridine versions, and the *n*-Pn, benzyl combination wingtip proved to give the highest activity. The catalytic system shows activity in the following competitive order: aldehyde > ketone > imine. This system has the added advantage of using a mild base such as K_2CO_3. Future studies will probe mechanistic details and try to improve the scope of the reductive amination step.

Experimental Section

1-Butyl-1,2,4-triazole,[42] 1-neopentyl-1,2,4-triazole,[43] and [Ir(cod)Cl]$_2$[44] were synthesized as previously described. All of the subsequent syntheses were performed in air (unless otherwise noted), using reagent grade solvents, which were used as received without further purification. All of the compounds used in the syntheses were obtained from Aldrich and Strem and were used as received. All of the catalytic runs were conducted under an atmosphere of argon using standard Schlenk techniques. NMR spectra were recorded at room temperature in $CDCl_3$ on a 400 MHz (operating at 162 MHz for ^{31}P) Bruker spectrometer and referenced to the residual solvent peak (δ in ppm and J in Hz). Elemental analyses were performed by Atlantic Microlab Inc. Solvents of crystallization were detected by ^{1}H NMR spectroscopy.

1-Butyl-4-benzyl-1,2,4-triazolium Bromide (1a). 1-Butyltriazole (1.565 g, 12.52 mmol) and benzyl bromide (2.140 g, 12.52 mmol) were added to toluene (10 mL), and the mixture was refluxed in air for 16 h. After this mixture was cooled, ether (30 mL) was added and the white solid that formed was filtered, washed with ether, and air-dried. Yield: 1.495 g (41%). ^{1}H NMR: δ 11.78 (s, 1 H, N−C$_5$H−N), 8.84 (s, 1 H, N−C$_3$H−N), 7.69−7.63 (m, 2 H, H arom), 7.44−7.38 (m, 3 H, H arom), 5.88 (s, 2 H, CH$_2$Ph), 4.43 (t, $^3J_{H-H}$ = 7.4, 2 H, CH$_2$ of *n*-Bu), 1.98 (m, 2 H, CH$_2$ of *n*-Bu), 1.40 (m, 2 H, CH$_2$ of *n*-Bu), 0.98 (t, $^3J_{H-H}$ = 7.4, 3 H, CH$_3$ of *n*-Bu). ^{13}C NMR: δ 143.31 (N−CH−N), 142.70 (N−CH−N), 132.13, 129.93, 129.68, 129.49 (C arom), 52.78 (CH$_2$Ph), 51.93 (N−CH$_2$ of *n*-Bu), 30.69 (CH$_2$ of *n*-Bu), 19.46 (CH$_2$ of *n*-Bu), 13.36 (CH$_3$ of *n*-Bu). Anal. Calcd for $C_{13}H_{18}N_3Br$ (296.21): C, 52.71; H, 6.12; N, 14.19. Found: C, 52.74; H, 6.10; N, 14.21.

1-Neopentyl-4-butyl-1,2,4-triazolium Bromide (1b). 1-Neopentyltriazole (1.501 g, 10.77 mmol) and *n*-butyl bromide (2.903 g, 21.16 mmol) were added to toluene (15 mL), and the mixture was refluxed under argon in the dark for 48 h. After this mixture was cooled, ether (50 mL) was added, and the white solid that formed was filtered, washed with ether, and air-dried. Yield: 508 mg (18%). ^{1}H NMR: δ 11.99 (s, 1 H, N−C$_5$H−N), 8.64 (s, 1 H, N−C$_3$H−N), 4.59 (t, $^3J_{H-H}$ = 7.5, 2 H, N−CH$_2$ of *n*-Bu), 4.35 (s, 2 H, CH$_2$ of *n*-Pn), 2.02 (m, 2 H, CH$_2$ of *n*-Bu), 1.42 (m, 2 H, CH$_2$ of *n*-Bu), 1.06 (s, 9 H, CH$_3$ of *n*-Pn). 1.01 (t, $^3J_{H-H}$ = 7.3, 3 H, CH$_3$ of *n*-Bu). ^{13}C NMR: δ 144.02 (N−C$_3$H−N), 142.62 (N−C$_5$H−N), 63.52 (CH$_2$ of *n*-Pn), 48.63 (NCH$_2$ of *n*-Bu), 32.70 (CMe$_3$ of *n*-Pn), 32.06 (CH$_2$ of *n*-Bu), 27.26 (CH$_3$ of *n*-Pn), 19.47 (CH$_2$ of *n*-Bu), 13.42 (CH$_3$ of *n*-Bu). Anal. Calcd for $C_{11}H_{22}N_3Br$ (276.22): C, 47.83; H, 8.03; N, 15.21. Found: C, 47.59; H, 7.98; N, 15.06.

1-Neopentyl-4-benzyl-1,2,4-triazolium Bromide (1c). This compound was prepared as for **1b**, except that the reaction time was 16 h and benzyl bromide was used. Yield: 66%. ^{1}H NMR: δ 11.73 (s, 1 H, N−C$_3$H−N), 9.31 (s, 1 H, N−C$_5$H−N), 7.75−7.72 (m, 2 H, H arom), 7.39−7.37 (m, 3 H, H arom), 5.94 (s, 2 H, CH$_2$Ph), 4.26 (s, 2 H, CH$_2$ of *n*-Pn), 1.01 (s, 9 H, CH$_3$ of *n*-Pn). ^{13}C NMR: δ 143.63 (N−C$_3$H−N), 143.12 (N−C$_5$H−N), 132.62, 129.79, 129.59, 129.38 (C arom), 63.47 (CH$_2$ of *n*-Pn), 51.65 (CH$_2$-Ph), 32.64 (CMe$_3$ of *n*-Pn), 27.23 (CH$_3$ of *n*-Pn). Anal. Calcd for $C_{14}H_{20}N_3Br$ (310.24): C, 54.20; H, 6.50; N, 13.54. Found: C, 54.20; H, 6.64; N, 13.49.

Transmetalation Reactions. General Procedure. A suspension of the appropriate triazolium bromide (**1a**−**c**; 1 mmol) and silver oxide (0.5 mmol) in CH_2Cl_2 was stirred at room temperature in the dark for 1.5 h. The mixture was then filtered through Celite (to remove unreacted silver oxide and any insoluble residues), and the resulting mixture was stirred with [Ir(cod)Cl]$_2$ (0.5 mmol) in the dark for 1.5 h. The suspension was filtered through Celite to remove the silver salts, and the solvent was removed under reduced pressure. The resulting solid was dried under vacuum and recrystallized from CH_2Cl_2/pentane.

{(1,2,5,6-η)-1,5-Cyclooctadiene}(1-butyl-4-benzyl-1,2,4-triazol-3-ylidene)chloroiridium (2a). Transmetalation was carried out in CH_2Cl_2 (15 mL) with **1a** (306 mg, 1.03 mmol), Ag_2O (128 mg, 0.55 mmol), and [Ir(cod)Cl]$_2$ (347 mg, 0.55 mmol). The product was a dark yellow solid. Yield: 551 mg (97%). ^{1}H NMR: δ 7.70 (s, 1 H, N−C$_3$H−N), 7.41−7.36 (m, 5 H, H arom), 5.68 (m, 2 H, CH of COD), 5.30 (s, 2 H, CH$_2$Ph), 4.73 (m, 2 H, CH of COD), 4.50 (t, $^3J_{H-H}$ = 7.6, 2 H, CH$_2$ of *n*-Bu), 2.97−2.82 (m, 2 H, CH$_2$ of COD), 2.25 (m, 2 H, CH$_2$ of COD), 2.08 (m, 2 H, CH$_2$ of COD), 1.96−1.84 (m, 2 H, CH$_2$ of COD), 1.80 (m, 2 H, CH$_2$ of *n*-Bu), 1.47 (m, 2 H, CH$_2$ of *n*-Bu), 1.01 (t, $^3J_{H-H}$ = 7.3, 3 H, CH$_3$ of *n*-Bu). ^{13}C NMR: δ 182.72 (Ir−C), 141.61 (N−C$_3$H−N), 134.75, 129.22, 128.76, 128.46 (C arom), 86.59, 86.45, 52.36, 51.48 (CH of COD), 52.45 (CH$_2$Ph), 52.20 (NCH$_2$ of *n*-Bu), 33.58, 33.42 (CH$_2$ of COD), 31.96 (CH$_2$ of *n*-Bu), 29.48, 29.39 (CH$_2$ of COD), 19.96 (CH$_2$ of *n*-Bu), 13.75 (CH$_3$ of *n*-Bu). Anal. Calcd for $C_{21}H_{29}N_3ClIr$ (551.15): C, 45.76; H, 5.30; N, 7.62. Found: C, 45.42; H, 5.28; N, 7.17.

[(1,2,5,6-η)-1,5-Cyclooctadiene](1-neopentyl-4-butyl-1,2,4-triazol-3-ylidene)chloroiridium (2b). Transmetalation was carried out in CH_2Cl_2 (15 mL) with **1b** (336 mg, 1.22 mmol), Ag_2O (144 mg, 0.61 mmol), and [Ir(cod)Cl]$_2$ (404 mg, 0.61 mmol). The product was a dark yellow solid. Yield: 587 mg (91%). ^{1}H NMR: δ 7.87 (s, 1 H, N−C$_3$H−N), 4.61 (m, 2 H, N−CH$_2$ of *n*-Bu), 4.51 (m, 2 H, CH of COD), 4.38 (m, 2 H, CH of COD), 4.14 (s, 2 H, CH$_2$ of *n*-Pn), 2.87 (m, 2 H, CH$_2$ of COD), 2.23 (m, 2 H, CH$_2$ of *n*-Bu), 2.20, 1.58, 1.44 (m, 6 H, CH$_2$ of COD), 1.46 (m, 2 H, CH$_2$ of *n*-Bu), 1.09 (s, 9 H, CH$_3$ of *n*-Pn), 1.02 (t, $^3J_{H-H}$ = 7.4, 3 H, CH$_3$ of *n*-Bu). ^{13}C NMR: δ 183.52 (Ir−C), 141.37 (N−C$_3$H−N), 86.06, 85.48 (CH of COD), 63.32 (CH$_2$ of *n*-Pn), 52.52, 51.68 (CH of COD), 48.27 (N−CH$_2$ of *n*-Bu), 33.94, 32.95 (CH$_2$ of COD), 32.61 (CMe$_3$ of *n*-Pn), 30.04 (CH$_2$ of *n*-Bu), 28.98, 28.77 (CH$_2$ of COD), 28.63 (CH$_3$ of *n*-Pn), 19.94 (CH$_2$ of *n*-Bu), 13.71 (CH$_3$ of *n*-Bu). Anal. Calcd for $C_{19}H_{33}N_3ClIr$ (531.16): C, 42.96; H, 6.26; N, 7.91. Found: C, 42.71; H, 6.17; N, 7.63.

[(1,2,5,6-η)-1,5-Cyclooctadiene](1-neopentyl-4-benzyl-1,2,4-triazol-3-ylidene)chloroiridium (2c). This compound was prepared in a manner analogous to that for **2b**. **1c** (400 mg, 1.29 mmol), Ag_2O (150 mg, 0.65 mmol), and [Ir(cod)Cl]$_2$ (425 mg, 0.65 mmol) were combined in CH_2Cl_2 (15 mL). The product was a bright yellow solid. Yield: 598 mg (85%). ^{1}H NMR: δ 7.73 (s, 1 H, N−C$_3$H−N), 7.42−7.36 (m, 5 H, H arom), 5.68 (m, 2 H, CH of COD), 4.80 (s, 2 H, CH$_2$ of *n*-Pn), 4.65 (m, 2 H, CH of COD), 4.15 (s, 2 H, CH$_2$Ph), 2.85 (m, 2 H, CH$_2$ of COD), 2.23−1.83 (m, 6 H, CH$_2$ of COD), 1.01 (s, 9 H, CH$_3$ of *n*-Pn). ^{13}C NMR: δ 183.74 (Ir−C), 141.49 (N−C$_3$H−N), 134.87, 129.52, 128.66, 128.03 (C arom), 86.34, 86.02 (CH of COD), 63.27 (CH$_2$ of *n*-Pn), 52.91 (CH$_2$Ph), 52.18, 51.78 (CH of COD), 33.76 (CMe$_3$ of *n*-Pn), 33.00, 32.64, 29.93, 28.93 (CH$_2$ of COD), 28.64 (CH$_3$ of *n*-Pn). Anal. Calcd for $C_{22}H_{31}N_3ClIr$ (565.18): C, 46.75; H, 5.53; N, 7.43. Found: C, 46.45; H, 5.50; N, 7.28.

General Procedure for Synthesis of Complexes 3a,b and **4a**−**c.** A suspension of the appropriate complex **2a**−**c**, pyridine (for

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3a,**b**) or triphenylphosphine (for **4a**−**c**), and $AgBF_4$ in CH_2Cl_2 was stirred at room temperature in the dark for 1.5 h under argon. The immediate formation of a white precipitate was observed. Then the mixture was filtered through Celite to remove silver chloride and any insoluble residues. The solvent was removed from the filtrate under reduced pressure. The residue was washed thoroughly with pentane and dried under vacuum. The resulting solids were recrystallized in CH_2Cl_2/pentane.

[(1,2,5,6-η)-1,5-Cyclooctadiene](1-butyl-4-benzyl-1,2,4-triazol-3-ylidene)(pyridine)iridium(I) Tetrafluoroborate (3a). Pyridine (81 mg, 1.02 mmol) and $AgBF_4$ (197 mg, 1.01 mmol) were added to **2a** (553 mg, 1.01 mmol) in degassed CH_2Cl_2 (15 mL). The product was a dark yellow solid. Yield: 630 mg (92%). ^{1}H NMR: 8.44 (d, $^3J_{H-H}$ = 5.1, 2 H, H of pyridine), 8.03 (s, 1 H, N−C_3H−N), 7.50 (m, 1 H, H of pyridine), 7.43−7.32 (m, 5H, H arom), 7.18 (m, 2 H, H of pyridine), 5.88 (m, 1 H, CH of COD), 5.40 (s, 2 H, NCH_2Ph), 5.62, 4.77 (m, 2 H, CH of COD), 4.52 (m, 2 H, NCH_2 of *n*-Bu), 4.17 (m, 1 H, CH of COD), 4.16, 3.99, 3.69, 3.50, 2.35 (m, 7 H, CH_2 of COD), 1.84 (m, 2 H, CH_2 of *n*-Bu), 1.63 (m, 1 H, CH_2 of COD), 1.45 (m, 2 H, CH_2 of *n*-Bu), 0.98 (t, $^3J_{H-H}$ = 7.3, 3 H, CH_3 of *n*-Bu). ^{13}C NMR: δ 179.60 (Ir−C), 151.69, 150.43 (C of pyridine), 144.08 (N−C_3H−N), 138.46, 135.47 (C of pyridine), 129.35, 128.68, 127.39, 126.95, 125.10 (C arom), 86.08, 85.39, 65.54, 62.98 (CH of COD), 52.73 (CH_2Ph), 51.75 (NCH_2 of *n*-Bu), 33.32 (CH_2 of *n*-Bu), 31.96, 31.61, 30.61, 29.09 (CH_2 of COD), 19.92 (CH_2 of *n*-Bu), 13.82 (CH_3 of *n*-Bu). Anal. Calcd for $C_{26}H_{34}N_4F_4BIr$ (681.61): C, 45.82; H, 5.03; N, 8.22. Found: C, 45.92; H, 5.05; N, 8.23.

[(1,2,5,6-η)-1,5-Cyclooctadiene](1-neopentyl-4-butyl-1,2,4-triazol-3-ylidene)pyridineiridium(I) Tetrafluoroborate (3b). Pyridine (72 mg, 0.91 mmol) and $AgBF_4$ (165 mg, 0.85 mmol) were added to **2b** (450 mg, 0.85 mmol) in degassed CH_2Cl_2 (15 mL). The product was a dark yellow solid. Yield: 461 mg (83%). ^{1}H NMR: δ8.65 (d, $^3J_{H-H}$ = 5.18, 2 H, H of pyridine), 8.15 (s, 1 H, N−C_3H−N), 7.80 (m, 1 H, H of pyridine), 7.60 (m, 2 H, H of pyridine), 4.92, 4.53 (m, 2 H, CH of COD), 4.36 (m, 2 H, CH_2 of *n*-Bu), 4.25 (s, 2 H, CH_2 of *n*-Pn), 4.20, 4.15, 3.71, 3.52 (m, 2 H, CH of COD), 2.37 (m, 2 H, CH_2 of COD), 2.32 (m, 2 H, CH_2 of *n*-Bu), 2.02, 1.83 (m, 6H, CH_2 of COD), 1.54 (m, 2 H, CH_2 of *n*-Bu), 1.04 (t, $^3J_{H-H}$ = 7.3, 3 H, CH_3 of *n*-Bu), 0.96 (s, 9 H, CH_3 of *n*-Pn). ^{13}C NMR: δ 179.81 (Ir−C), 150.88 (C of pyridine), 142.71 (N−C_3H−N), 138.77, 127.17 (C of pyridine), 85.82, 84.46, 64.67, 63.50 (CH of COD), 63.15 (CH_2 of *n*-Pn), 48.46 (N−CH_2 of *n*-Bu), 33.48, 33.02 (CH_2 of COD), 32.29 (CMe_3 of *n*-Pn), 31.38, 30.82 (CH_2 of COD), 28.98 (CH_2 of *n*-Bu), 28.23 (CH_3 of *n*-Pn), 19.96 (CH_2 of *n*-Bu), 13.78 (CH_3 of *n*-Bu). Anal. Calcd for $C_{24}H_{38}N_4F_4BIr$ (661.62): C, 43.57; H, 5.79; N, 8.47. Found: C, 43.32; H, 5.79; N, 8.24.

[(1,2,5,6-η)-1,5-Cyclooctadiene](1-butyl-4-benzyl-1,2,4-triazol-3-ylidene)(triphenylphosphine)iridium(I) Tetrafluoroborate (4a). Triphenylphosphine (214 mg, 0.82 mmol) and $AgBF_4$ (158 mg, 0.82 mmol) were added to **2a** (450 mg, 0.82 mmol) in degassed CH_2Cl_2 (15 mL). The product was a bright orange solid. Yield: 595 mg (85%). ^{1}H NMR: δ 7.94 (s, 1 H, N−C_3H−N), 7.53−7.30 (m, 20 H, H_{ar}), 5.30 (s, 2 H, CH_2Ph), 5.42, 5.38, 4.84, 4.80 (m, 4 H, CH of COD), 4.45 (m, 2 H, NCH_2 of *n*-Bu), 2.35 (m, 5 H CH_2 of COD), 2.17 (m, 2 H, CH_2 of *n*-Bu), 2.03 (m, 3 H, CH_2 of COD), 1.33 (m, 2 H, CH_2 of *n*-Bu), 0.90 (t, $^3J_{H-H}$ = 7.6, 3 H, CH_3 of *n*-Bu). ^{13}C NMR: δ 178.20 (Ir−C), 143.98 (N−C_3H−N), 133.71−127.03 (C arom), 87.38, 87.37, 86.75, 86.63 (CH of COD), 52.69 (N−CH_2 of *n*-Bu), 52.15 (CH_2Ph), 31.67, 31.02, 30.72, 30.61 (CH_2 of COD), 30.26 (CH_2 of *n*-Bu), 20.07 (CH_2Me of *n*-Bu), 13.69 (CH_3 of *n*-Bu). ^{31}P NMR: δ 18.54. Anal. Calcd for $C_{39}H_{44}N_3F_4BPIr$ (864.79): C, 54.17; H, 5.13; N, 4.86. Found: C, 54.06; H, 5.10; N, 4.85.

[(1,2,5,6-η)-1,5-Cyclooctadiene](1-neopentyl-4-butyl-1,2,4-triazol-3-ylidene)(triphenylphosphine)iridium(I) Tetrafluoroborate (4b). Triphenylphosphine (151 mg, 0.58 mmol) and $AgBF_4$ (112 mg, 0.58 mmol) were added to **2b** (306 mg, 0.58 mmol) in degassed CH_2Cl_2 (10 mL). The product was a bright orange-red solid. Yield: 453 mg (93%). ^{1}H NMR: 8.32 (s, 1 H, N−C_3H−N), 7.54−7.23 (m, 15 H, H arom), 4.28 (s, 2 H, CH_2 of *n*-Pn), 4.25 (m, 2 H, CH_2 of *n*-Bu), 4.18, 2.92, 2.89 (m, 4 H, CH of COD), 2.39, 2.29 (m, 6 H, CH_2 of COD), 2.18, (m, CH_2 of *n*-Bu), 1.64 (m, 2 H, CH_2 of COD), 1.42 (m, 2 H, CH_2Me of *n*-Pn), 0.99 (s, 9 H, CH_3 of *n*-Pn), 0.98 (t, $^3J_{H-H}$ = 7.2, 3 H, CH_3 of *n*-Bu). ^{13}C NMR: δ 178.73 (Ir−C), 143.75 (N−C_3H−N), 133.64−129.09 (C arom), 86.53, 81.19, 80.98 (CH of COD), 63.29 (CH_2 of *n*-Pn), 48.62 (N−CH_2 of *n*-Bu), 32.22 (CMe_3 of *n*-Pn), 31.80, 31.36, 30.92 (CH_2 of COD), 30.32 (CH_2 of *n*-Bu), 28.54 (CMe_3 of *n*-Pn), 20.03 (CH_2Me of *n*-Bu), 13.65, (CH_3 of *n*-Pn). ^{31}P NMR: δ 18.67. Anal. Calcd for $C_{37}H_{48}N_3F_4BPIr$ (844.80): C, 52.61; H, 5.73; N, 4.97. Found: C, 52.44; H, 5.71; N, 4.76.

[(1,2,5,6-η)-1,5-Cyclooctadiene](1-neopentyl-4-benzyl-1,2,4-triazol-3-ylidene)(triphenylphosphine)iridium(I) Tetrafluoroborate (4c). Triphenylphosphine (181 mg, 0.68 mmol), and $AgBF_4$ (133 mg, 0.68 mmol) were added to **2c** (386 mg, 0.68 mmol) in degassed CH_2Cl_2 (15 mL). The product was a bright orange solid. Yield: 615 mg (99%). ^{1}H NMR: δ 8.03 (s, 1 H, N−C_3H−N), 7.55−7.29 (m, 20 H, H arom), 5.48, 4.91, 4,58, 4.28 (m, 4 H, CH of COD), 5.30 (s, 2 H, CH_2 of *n*-Pn), 4.27 (s, 2 H, CH_2Ph), 3.04, 2.34−1.98 (m, 8 H, CH_2 of COD), 1.00 (s, 9 H, CH_3 of *n*-Pn). ^{13}C NMR: δ 179.97 (Ir−C), 144.00 (N−C_3H−N), 133.93−128.11 (C arom), 82.52, 82.17, 63.58 (CH of COD), 53.50 (CH_2 of *n*-Pn), 52.20 (CH_2Ph), 32.25 (CMe_3 of *n*-Pn), 31.32, 30.89, 30.68, 30.55 (CH_2 of COD), 28.56 (CH_3 of *n*-Pn). ^{31}P NMR: δ 18.41. Anal. Calcd for $C_{40}H_{46}N_3F_4BPIr$ (878.82): C, 54.66; H, 5.27; N, 4.78. Found: C, 54.65; H, 5.39; N, 4.76.

General Procedure for Catalytic Reduction of All Unsaturated Substrates. An oven-dried flask was charged with 1 mmol of substrate, 0.5 equiv of K_2CO_3, 1,3,5-tri-*tert*-butylbenzene as internal standard, and the appropriate catalyst **3** or **4** at 1.0 mol % loading. The flask was evacuated and filled with N_2, 10 mL of dry, degassed *i*-PrOH was added, and the mixture was refluxed for 30 min. An aliquot (0.5 mL) of the mixture was quenched with 2 mL of pentane, and the resulting solution was filtered through Celite to remove insoluble inorganic material. The volatiles were then removed under vacuum, and the conversion was checked with ^{1}H NMR. The conversion is based on moles of substrate and comparison to internal standard. The data reported are based on an average of two catalytic runs.

General Procedure for Reductive Amination. An oven-dried flask was charged with 1 mmol of the appropriate aldehyde and an amine (see Table 2), together with 0.5 equiv of K_2CO_3 and 1,3,5-tri-*tert*-butylbenzene as internal standard. The flask was evacuated and refilled with N_2, 10 mL of degassed and dry *i*-PrOH (or cyclopentanol) was added, and the mixture was stirred at room temperature until the imine was formed (checked with ^{1}H NMR). After the imine was formed, catalyst **4b** was added under a steady flow of nitrogen and the mixture was refluxed for 24 h. An aliquot of the mixture was then quenched with 2 mL of pentane, and the resulting solution was filtered through Celite. The volatiles were then removed under vacuum and the conversion checked with ^{1}H NMR. The conversion is based on moles of substrate and comparison to internal standard. The data reported are based on an average of two catalytic runs.

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