Cationic Iridium Complexes Bearing Imidazol-2-ylidene Ligands as Transfer Hydrogenation Catalysts

Anna C. Hillier, Hon Man Lee, Edwin D. Stevens, and Steven P. Nolan*

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

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The synthesis and characterization by X-ray crystallography of the complexes [Ir(cod)(py)(L)]PF_6 (L = IMes, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (**2**); L = IPr, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**3**); L = ICy, 1,3-bis(cyclohexyl)imidazol-2-ylidene (**4**)) are reported. Complexes **2**−**4** have been employed as catalysts for transfer hydrogenation reactions from 2-propanol to a number of unsaturated substrates and their activity compared with that of the related cationic iridium(I) species [Ir(cod)(py)(SIMes)]PF_6 (**1**), [Ir(cod)(py)(PCy_3)]PF_6 (**5**), and complexes formed in situ from [Ir(cod)$(py)_2$]PF_6 and diazabutadienes (RN=CHCH=NR, DAB-R; R = cyclohexyl, DAB-Cy; R = 2,4,6-trimethylphenyl, DAB-Mes; R = adamantyl, DAB-Ad; R = 2,4,6-trimethoxyphenyl, DAB-trimethoxyphenyl). All complexes tested were found to be active catalysts for transfer hydrogenation of ketones, with complex **4** displaying the highest activity. Complex **4** also exhibits moderate activity toward simple olefins and an aromatic nitro compound.

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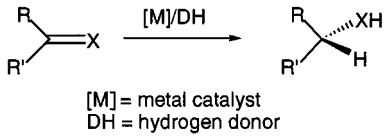
Introduction

The reduction of organic compounds is an important synthetic process both in the laboratory and in industry. Reduction of multiple bonds via addition of hydrogen from an inorganic or organic hydrogen donor (i.e. other than gaseous hydrogen) is known as hydrogen transfer or transfer hydrogenation (Scheme 1).[1]

Transfer hydrogenation can be activated thermally, photochemically, or catalytically,[2,3] with much interest in catalytic processes owing to the mild conditions and generally good selectivity. Indeed, metal-catalyzed processes present significant practical advantages, particularly in large-scale synthesis, since there is no need to employ a high dihydrogen pressure or a hazardous reducing agent. Homogeneous catalysis offers the possibility of fine-tuning the properties of the catalyst in order to enhance selectivity. Organometallic complexes of ruthenium have been well-employed to this effect, recently in particular by the groups of Noyori[4] and Braunstein.[5] Iridium and rhodium complexes have long been known to be highly effective homogeneous hydrogenation catalysts, with $RhCl(PPh_3)_3$ (Wilkinson's catalyst)[6] and [Ir(cod)(py)(PCy_3)]PF_6 (py = pyridine, cod = 1,5-cyclooctadiene; **5**, Crabtree's catalyst)[7] the most widely used. The use of related cationic complexes [Ir(cod)$(L)_2$]$^+$ (L = N- or P-donor ligand) and iridium(III) compounds as *transfer* hydrogenation catalysts is also well-documented, with activity and selectivity dependent on the steric and electron donor properties of the ancillary ligands (L).[8]

Scheme 1



Nucleophilic carbenes have been demonstrated to be thermally stable alternatives to the widely used phos-

* To whom correspondence should be addressed. E-mail: snolan@uno.edu.

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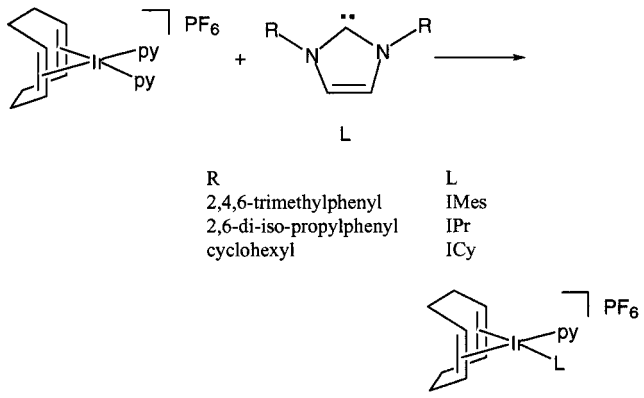
Scheme 2



phine ligands in metal complexes employed in homogeneous catalysis.[9] It was, therefore, of interest to determine whether replacement of P- and N-donor ligands by carbenes in cationic iridium complexes would afford active hydrogenation catalysts. The iridium complex [Ir(cod)(py)(SIMes)]PF_6 (**1**), where SIMes is the nucleophilic N-heterocyclic carbene 4,5-dihydro-1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene, has recently been reported as a thermally stable analogue of Crabtree's catalyst.[10] We now report the synthesis of the related complexes [Ir(cod)(py)(L)]PF_6, where L is an unsaturated nucleophilic carbene (L = IMes, 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene (**2**); L = IPr, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**3**); ICy, 1,3-bis(cyclohexyl)imidazol-2-ylidene (**4**)), and the results of investigations into their activity as homogeneous *transfer* hydrogenation catalysts.

Results and Discussion

Synthesis and Characterization of [Ir(cod)(py)(L)]PF_6 (L = IMes (2), IPr (3), ICy (4)). Complexes **2**−**4** were prepared by a simple ligand exchange reaction of [Ir(cod)$(py)_2$]PF_6 with a small excess of carbene in toluene (Scheme 2). In the case of **4**, the free carbene was not isolated but prepared and used in situ by the reaction of ICy·HCl with KO^{t}Bu in THF. The generated carbene was then extracted into toluene and treated directly with [Ir(cod)$(py)_2$]PF_6. Two days of stirring at room temperature afforded a yellow or orange solid which could be isolated by filtering and washing with hexane or toluene.[11]

The ^{1}H NMR spectrum of **4** displays two multiplets at δ 3.87 and 3.93 ppm for the cod vinyl hydrogens (Table 1). Complexes **2** and **3** exhibit the cod vinyl proton resonances at δ 3.64 and 3.20 and at δ 3.63 and 3.04 ppm, respectively. The downfield signal for the cod vinyl hydrogens ($\delta(H_A)$) in [Ir(cod)(py)(L)]PF_6 (L = monophosphine) has been previously demonstrated to belong to the protons of the cod double bond trans to L.[7b] By analogy, we assign the upfield resonances in compounds **2**−**4** to the cod vinyl hydrogens trans to pyridine and the downfield resonances to those trans to the carbene ligand. Crabtree and Morris correlated the $\delta(H_A)$ value to the trans influence of the phosphine ligand in [Ir(cod)(py)(L)]PF_6. Although trans influence is not the only factor affecting $\delta(H_A)$, within this series of compounds where only L varies, a weaker trans influence of the nucleophilic carbene ligands compared to that of monophosphines is suggested by the upfield shifts observed for $\delta(H_A)$ in **2**−**4**, compared to **5** (at δ 4.13 and 3.91 ppm). ICy in **4** appears to behave as the strongest trans-influence carbene in the series examined.

Complexes **2** and **3** display fluxional behavior in solution, via rotation about the carbene N−C(Ar) bond. At room temperature the ^{1}H NMR spectrum of **2** exhibits only broad resonances for the mesityl *o*-methyl groups and the phenyl ring hydrogens. Cooling the sample to 233 K freezes out two *o*-CH_3 (Mes) and two Mes CH environments. No change is observed on further cooling. The resonances associated with the IPr ligand in the room-temperature ^{1}H NMR spectrum of **3** are similarly very broad. When the temperature is lowered to 233 K, four doublets (^{i}Pr CH_3) and two multiplets (^{i}Pr CH) emerge, as well as two broad singlets for the IPr phenyl ring meta hydrogens.

X-ray Analysis of 2−4. Crystals of compounds **2**−**4** suitable for X-ray diffraction studies were grown by slow diffusion of diethyl ether into a dichloromethane solution of the complex. The ORTEP diagrams of **2**−**4** are presented in Figures 1−3, and selected bond lengths and angles for **2**−**4**, together with those for **1** for comparison, are given in Table 3.

Complexes **2**−**4** exhibit square planar geometry at iridium, taking the cyclooctadiene C═C midpoints as vertexes. The Ir−C(carbene) distance in **4** is slightly shorter than that in **1**−**3**, presumably due to a combination of steric and electronic effects which favors a stronger Ir−carbene interaction for ICy. The Ir−N(pyridine) bond is also marginally longer in **4** than in **2** and **3**, pointing to ICy being a better σ-donor ligand. The weak trans influence of the carbene ligand is evident in the Ir−C(cod) bond distances for the cod vinyl carbons trans to the carbene, which are up to 0.07 Å longer than those trans to pyridine. These observations are also in accord with the small downfield shift of the cod vinyl hydrogen resonances in the NMR spectra of complexes **2**−**4**. The Ir−(C═C) interaction is somewhat unsymmetric in compounds **1**−**3**, with one Ir−C bond shorter than the other. The same interaction in **4**, on the other hand, appears symmetrical, with two roughly equivalent Ir−C bond lengths. Indeed, the shorter Ir−C(cod *t*-carbene) distance in **2** and **3** is equivalent to Ir−C(cod, *t*-pyridine), whereas the second Ir−C(cod *t*-carbene) bond is longer than the Ir−C(cod *t*-carbene) distance in **4**. In complexes **1** and **4** the C═C(cod) distance for the bond trans to carbene is slightly shorter than that trans

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(11) These reactions are rather slow, and in some preparations varying amounts of the starting iridium complex can remain. In the case of IMes and IPr very small amounts of a second product, containing cod and carbene but no pyridine, were obtained. The exact composition of these compounds has not yet been fully elucidated. Additionally, there is some evidence for lability of one or more ligands in **2**−**4** from NMR studies on samples kept in solution for several weeks. A study aimed at understanding the solution behavior of these complexes is ongoing.

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Table 1. Selected ^{1}H and ^{13}C NMR Spectral Data (ppm; in CD_2Cl_2) for [Ir(cod)(py)L]PF_6 (L = SIMes (1), IMes (2), IPr (3), ICy (4))

	1[9]	2	3	4
^{1}H, $\delta(H_A)$ (cod vinyl H)	3.80 (*t*-carbene), 3.15 (*t*-py)	3.64 (*t*-carbene), 3.20 (*t*-py)	3.63 (*t*-carbene), 3.04 (*t*-py)	3.93 (*t*-carbene), 3.87 (*t*-py)
^{13}C, carbene	201.58	173.95	175.56	174.87

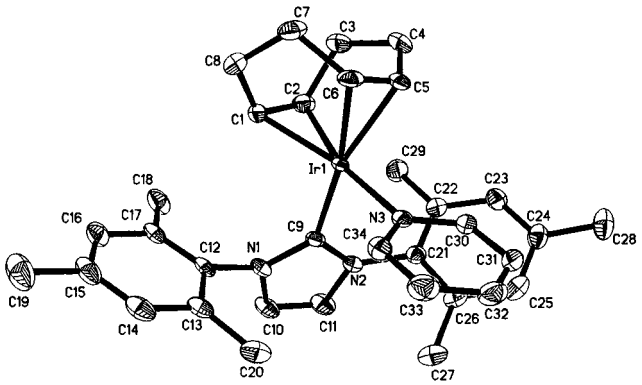

Figure 1. ORTEP diagram of [Ir(cod)(py)(IMes)]PF_6 (**2**) with ellipsoids drawn at 50% probability. The PF_6 counterion has been omitted for clarity.

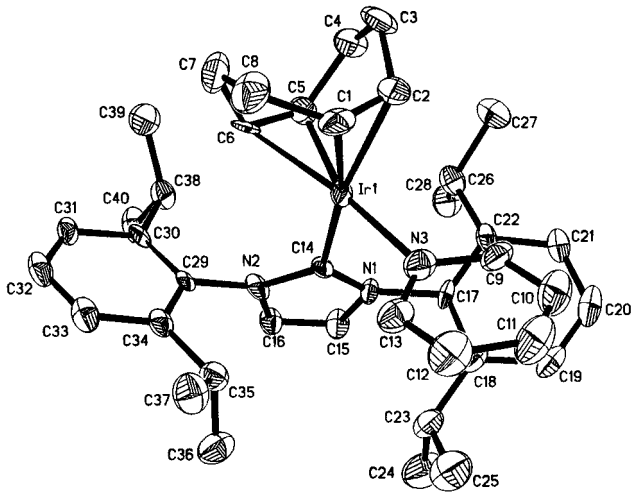

Figure 2. ORTEP diagram of [Ir(cod)(py)(IPr)]PF_6 (**3**) with ellipsoids drawn at 50% probability. The PF_6 counterion has been omitted for clarity.

to pyridine, as expected for a longer, weaker Ir−C(cod) (and hence stronger C═C(cod)) interaction. Complexes **2** and **3**, on the other hand, display effectively the same bond distances for the C═C bonds trans to carbene and to pyridine.

While no completely clear overall picture emerges regarding the bonding in these complexes, the X-ray and NMR spectroscopic data do suggest that ICy is a better σ-donor and trans influence ligand than IMes, IPr, or SIMes in this cationic iridium system. This could be expected on the basis of electronic parameters, since cyclohexyl is a better electron donor than the aromatic imidazole N substituents mesityl and 2,6-diisopropylphenyl, resulting in increased electron density on the carbene carbon. The availability of the carbene lone pair is also affected by the steric properties of the ligand.[8c,10] Presumably the reduced steric demand of the ICy system, compared to the 2,6-(disubstituted phenyl) N substituents on the imidazole ring in IMes and IPr, also contributes to a stronger Ir−C(carbene) interaction in

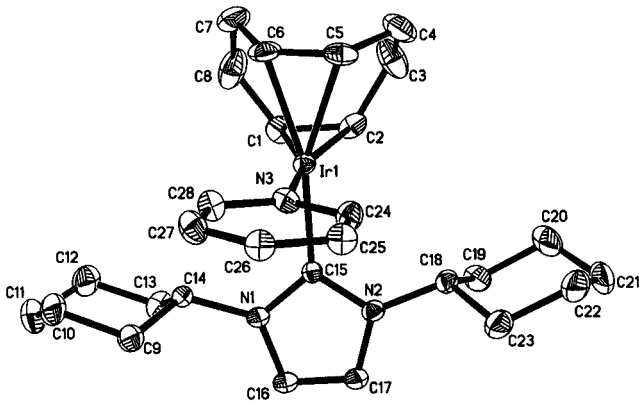

Figure 3. ORTEP diagram of [Ir(cod)(py)(ICy)]PF_6 (**4**) with ellipsoids drawn at 50% probability. The PF_6 counterion has been omitted for clarity.

4. Solution calorimetric results in the Cp*RuCl(L) system clearly indicate the increased donor properties of the ICy ligand over IMes and IPr.[11]

Catalytic Transfer Hydrogenation. Complexes **1**−**5**, together with their precursors $[Ir(cod)Cl]_2$ and [Ir(cod)$(py)_2$]PF_6 and complexes formed in situ from [Ir(cod)$(py)_2$]PF_6 and diazabutadiene ligands[13] (RN═CHCH═NR, DAB−R; R = cyclohexyl, DAB-Cy; R = 2,4,6-trimethylphenyl, DAB-Mes; R = adamantyl, DAB-Ad; R = 2,4,6-trimethoxyphenyl, DAB-trimethoxyphenyl) for comparison, were tested for catalytic activity in the hydrogen transfer reduction of cyclohexanone to cyclohexanol, employing 2-propanol as hydrogen donor. The required activation time was 30 min and involved heating a solution of catalyst and base (KOH) in 2-propanol at 80 °C, which was followed by addition of the substrate. The catalytic results are given in Table 4.

The use of $[Ir(cod)Cl]_2$ as catalyst (entry 2) resulted in only a slight improvement of the reaction rate compared to that obtained when the reaction was carried out in the presence of base with no catalyst (entry 1). In addition, the initial step appeared to be formation of metallic iridium, with the pale yellow solution decolorizing and a fine black precipitate forming after 15 min of initial heating at 80 °C. [Ir(cod)$(py)_2$]PF_6, on the other hand, afforded modest reaction rates (entry 3), suggesting that either the monomeric or the cationic nature of the complex is essential to catalytic activity. The in situ formed diazabutadiene complexes displayed moderate catalytic activity (entries 4−7), in particular with the better electron donor and less bulky cyclohexyl and adamantyl substituents. Their catalytic ability was, however, a little disappointing compared to the high activity reported for some similar Ir(I) systems possessing chelating bidentate N-donor li-

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Table 2. X-ray Data for [Ir(cod)(py)L]PF_6 (L = IMes (2), IPr (3), ICy (4))

	2	3	4
empirical formula	$(C_{34}H_{41}IrN_3)^+(PF_6)^-$	$(C_{41}H_{53}IrN_3)^+(PF_6)^-\cdot 0.25C_4H_{10}O$	$(C_{28}H_{41}IrN_3)^+(PF_6)^-$
fw	828.87	931.55	756.81
cryst syst	triclinic	monoclinic	orthorhombic
space group	*P*1	*C*2/*c*	*Pbca*
a, Å	10.1336(6)	47.217(3)	19.2529(4)
b, Å	12.3401(7)	10.6421(7)	14.0152(3)
c, Å	13.8497(8)	39.915(3)	21.1527(5)
α, deg	83.247(2)	90	90
β, deg	73.640(2)	126.012(3)	90
γ, deg	81.261(2)	90	90
V (Å^3)	1637.37(16)	16223.7(19)	5707.7(2)
Z	2	16	8
D_{calcd} (Mg/m^3)	1.681	1.526	1.761
no. of rflns collected	54 564	46 946	85 800
no. of indep rflns	17 411 (*R*(int) = 0.0559)	11 690 (*R*(int) = 0.1378)	11 995 (*R*(int) = 0.0740)
no. of refined params	505	1079	507
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0314, wR2 = 0.0550	R1 = 0.0444, wR2 = 0.0882	R1 = 0.0263, wR2 = 0.0487
R indices (all data)	R1 = 0.0510, wR2 = 0.0564	R1 = 0.1008, wR2 = 0.0950	R1 = 0.0587, wR2 = 0.0515

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [Ir(cod)(py)L]PF_6 (L = SIMes (1), IMes (2), IPr (3), ICy (4))

	1[9]	2	3	4
		Bond Lengths		
Ir−C(carbene)	2.0743(18)	2.0762(19)	2.080(10)	2.062(2)
Ir−N	2.1073(16)	2.0954(17)	2.081(9)	2.1004(18)
Ir−C(cod *t*-carbene)	2.215(2)	2.136(2)	2.193(10)	2.170(2)
Ir−C(cod *t*-carbene)	2.1545(19)	2.193(2)	2.217(11)	2.180(2)
Ir−C(cod *t*-py)	2.144(2)	2.1259(19)	2.216(11)	2.136(2)
Ir−C(cod *t*-py)	2.1349(18)	2.137(2)	2.131(10)	2.135(2)
C−C (cod *t*-carbene)	1.391(3)	1.402(3)	1.408(15)	1.375(4)
C−C (cod *t*-py)	1.408(3)	1.399(3)	1.383(14)	1.400(4)
		Bond Angles		
N−Ir−C(carbene)	96.00(7)	94.45(7)	95.4(4)	90.78(7)
C(cod *t*-carbene)−Ir−C(carbene)	169.80(8)	170.12(8)	165.4(4)	164.44(10)
C(cod *t*-carbene)−Ir−C(carbene)	152.16(9)	151.59(8)	157.1(4)	158.70(10)
C(cod *t*-py)−Ir−C(carbene)	89.71(8)	93.25(8)	88.6(4)	92.77(9)
C(cod *t*-py)−Ir−C(carbene)	93.00(7)	90.13(8)	95.8(4)	92.00(9)
C(cod *t*-carbene)−Ir−N	88.21(7)	87.68(7)	85.6(4)	88.98(8)
C(cod *t*-carbene)−Ir−N	86.93(7)	88.73(7)	88.9(4)	90.59(9)
C(cod *t*-py)−Ir−N	164.45(7)	165.08(7)	159.5(4)	162.12(9)
C(cod *t*-py)−Ir−N	154.58(8)	154.83(8)	159.5(4)	159.04(9)

Table 4. Catalytic Hydrogen Transfer from 2-Propanol to Cyclohexanone by Cationic Iridium Complexes[a]

entry	catalyst	time, h	conversn, %[b]	TON, h^{-1}
1	none	5	10	
2	$[Ir(cod)Cl]_2$	5	20	8
3	$[Ir(cod)py_2]^+$	10	81	32
4	[Ir(cod)py(DAB-Cy)]$^+$	4.5	100[c]	75
5	[Ir(cod)py(DAB-Mes)]$^+$	22	83[c]	18
6	[Ir(cod)py(DAB-trimethoxyphenyl)]$^+$	22	67[c]	10
7	[Ir(cod)py(DAB-Ad)]$^+$	7.5	93[c]	25
8	[Ir(cod)py(SIMes)]$^+$	6	100	64
9	[Ir(cod)py(IMes)]$^+$	4.5	100	44
10	[Ir(cod)py(IPr)]$^+$	8	89	29
11	[Ir(cod)py(ICy)]$^+$	10 min	100	>1200[d]
12	[Ir(cod)py(SICy)]$^+$	5.5	84[e]	31
13	[Ir(cod)py(PCy_3)]$^+$	9	92	26

[a] Reaction conditions: 0.02 mmol catalyst (0.5 mol %), 0.2 mmol KOH, 4 mmol cyclohexanone, 20 mL 2-propanol, 80 °C, 30 min activation time. [b] GC yields. All reactions were monitored by GC. [c] Ir complex prepared in situ from 1 equiv of ligand with respect to $[Ir(cod)(py)_2]PF_6$. [d] See text. [e] Ir complex prepared in situ from SICy·HCl and $[Ir(cod)(py)_2]PF_6$.

gands.[8o,14] Surprisingly, given its well-documented thermal instability, Crabtree's catalyst was reasonably active in transfer hydrogenation under these conditions (entry 13). Removal of volatiles from the reaction mixture in this case afforded a yellow-brown oily material which displayed resonances in the hydride region of the ^{1}H NMR spectrum, consistent with formation of a bis(phosphine) metal hydride complex. These resonances did not, however, match those reported for the known hydride-bridged trinuclear decomposition product of $[\{Ir(H_2)py(PCy_3)\}_3(\mu_3\text{-}H)]^+$, and crystalline material could not be obtained. Of the carbene complexes **1**−**4** (entries 8−11), complex **4** was found to be the most reactive, with quantitative conversion of cyclohexanone to cyclohexanol within 10 min, even with a 2-fold increase in substrate/catalyst ratio (Table 5 entry 1). The complex [Ir(COD)(py)(SICy)]PF_6 (SICy = 4,5-dihydro-1,3-dicyclohexylimidazol-2-ylidene) might be expected to display higher activity, since the SICy ligand is a better electron donor than ICy. The lower activity observed could be due to the in situ preparation of the complex, although we note that in many reports the catalyst precursor is prepared in situ, occasionally affording more active catalytic species than the isolated complexes.[8g] We attribute the lower catalytic activity to an incomplete deprotonation and subsequent coordi-

(14) (a) Zassinovich, G.; Bettella, R.; Mestroni, G.; Bresciani-Pahor, N.; Geremia, S.; Randaccio, L. *J. Organomet. Chem.* **1989**, *370*, 187−202. (b) Zassinovich, G.; Camus, A.; Mestroni, G. *J. Mol. Catal.* **1980**, *9*, 345−347. (c) Bikrani, M.; Fidalgo, L.; Garralda, M. A.; Ubide, C. *J. Mol. Catal. A: Chem.* **1997**, *118*, 47−53.

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Table 5. Catalytic Hydrogen Transfer from 2-Propanol to Cyclohexanone by [Ir(cod)py(ICy)]$^+$ [a]

entry	*S/C*	time, h	conversn, %	TON, h^{-1}
1	400	10 min	100	2400
2	400	24	1[b]	
3	400	10 min	100[c]	2400
4	1000	4	100	300
5	2000	36	39	30

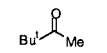
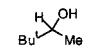
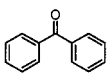
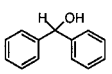
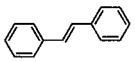
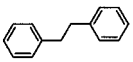
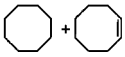
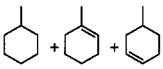
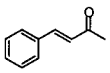
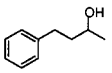
[a] Reaction conditions as for Table 4, except where noted. [b] No KOH added. [c] Solvent 2-butanol.

nation of the ligand to the metal center under catalyst generation conditions.

The activity of complex **4** was investigated under various conditions (Table 5). The same rapid reaction was observed when 2-butanol was employed as solvent (entry 3), with the turnover number (TON) probably exceeding the calculated value of 2400 h^{-1}, since the reaction was complete by the first GC measurement after the reaction had proceeded 10 min. A reaction with no added potassium hydroxide (entry 2) confirmed that the presence of base is essential to catalytic activity. Increasing the ratio of substrate to catalyst (*S/C*) resulted in slower reactions, with an *S/C* value of 1000 affording complete conversion in 4 h (entry 4), corresponding to a TON of 300 h^{-1} measured over the first hour (average TON 250 h^{-1} over the total reaction time). Further decreasing the *S/C* ratio to 2000 resulted in a TON of 30 h^{-1} (average over first 12 h). Since complex **4** displayed the highest activity of the complexes tested, it was investigated as a catalyst for hydrogen transfer from 2-propanol to a number of unsaturated substrates (Table 6).

At 0.025 mol % catalyst concentration (*S/C* = 400) rapid, quantitative conversion of simple ketones such as pinacolone (entry 1) and benzophenone (entry 2) is observed. Reaction with the simple olefins 1-hexene, cyclohexene, and *cis*-cyclooctene (entries 3−5) similarly results in conversion to the hydrogenated product, albeit with considerably longer reaction times than the ketones. In the case of 1-hexene, the possibility of isomerization of terminal to internal olefins was a concern. The difference in reactivity toward simple olefins and ketones should permit a reasonable degree of selectivity in hydrogen transfer to substrates containing nonconjugated C=C and C=O functionalities. Selective reduction of α,β-unsaturated ketones to afford allylic alcohols affords useful organic synthons. To test selective redution, benzylideneacetone (*trans*-4-phenyl-3-buten-2-one, entry 10) is employed as a standard.[15,16] The transfer hydrogenation of benzylideneacetone employing **4** as catalyst results in rather fast conversion to the saturated alcohol, 4-phenyl-2-butanol, within 5.5 h. Initial hydrogenation appears to occur at both the C=C and the C=O bonds, since two peaks are observed in the gas chromatograms over the first 3 h in approximately equal quantities, which correspond to addition of 2 H (*m/z* 148 in the GCMS). This is in contrast to a previous report, in which the saturated ketone is practically the only reaction product at low conversion, followed by rapid

Table 6. Transfer Hydrogenation Reactions with [Ir(cod)(py)ICy]PF_6 [a]

entry	substrate	product	time, h	conversion, %
1			35 min	100[c]
2			10 min	100
3			22	90
4			18.5	100
5			7	98
6			6	88
7			48	37
8			24 48	30 + 60 0 + 100
9			3 24	8 + 15 + 50 3 + trace +90
10			5.5	100
11			48	48

[a] Reaction conditions: 0.01 mmol catalyst (0.025 mol %), 0.2 mmol KOH, 4 mmol cyclohexanone, 20 mL 2-propanol, 80 °C, 30 min activation time. [b] Determined by GC analysis. [c] First analysis at 35 min.

conversion to the saturated alcohol.[16] The mechanism presumably involves a keto−enol tautomerization step, as proposed for the isomerization of unsaturated alcohols by [Ir(cod)(PPh_3)L]ClO_4 (L = nitrile).[17] Substrates containing more than one C=C double bond, on the other hand, generally afforded the singly hydrogenated product; i.e., the overall reaction is hydrogenation at only one double bond. *trans*-Stilbene is reduced slowly to 1,2-diphenylethane (entry 7), with no evidence for hydrogenation of the aromatic rings. Cyclooctadiene (entry 8) is initially hydrogenated to give a mixture containing equal amounts of cyclooctane and cyclooctene after 19 h, with quantitative conversion to cyclooctene in 48 h. Similarly, transfer hydrogenation of 1-methyl-1,4-cyclohexadiene (entry 9) initially affords a mixture of 1-methylcyclohexane, 1-methyl-1-cyclohexene, and 1-methyl-4-cyclohexene, with 1-methyl-4-cyclohexene emerging as the major product (90% by GC) after 24 h. This "partial hydrogenation" apparently results at least in part from initial hydrogenation to afford the fully saturated species, followed by hydrogen transfer from the saturated product to the substrate (or to the other possible unsaturated product, 1-methyl-1-cyclohexene), indicating that some activation of alkane C−H bonds with concomitant selective hydrogen transfer is occur-

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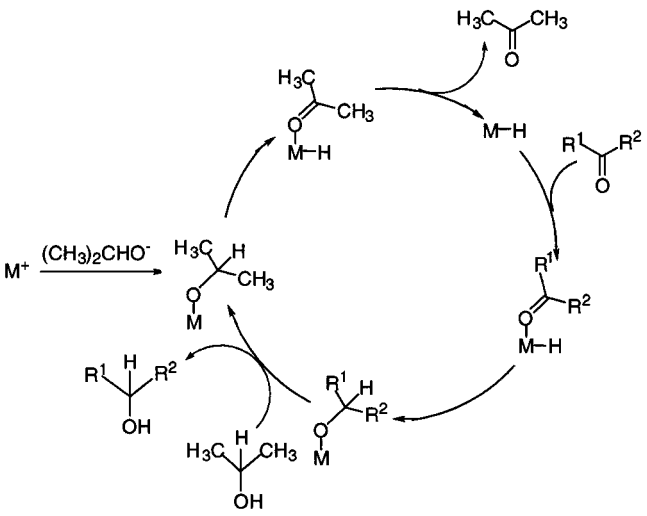
ring.[18] Complex **4** also catalyzes the slow transfer hydrogenation of the aromatic nitro compound 2-nitro-*m*-xylene to 3,5-dimethylaniline (entry 11), with 48% conversion in 48 h. This is somewhat slower than the reduction rates reported for nitroaromatic compounds by Ir(I) complexes with 2,2′-bipyridine and 1,10-phenanthroline ligands.[19]

No reaction was observed with phenylacetylene, *p*-tolunitrile, or the prochiral imine (2-OH)C_6H_4N=CH-(Me)C_6H_5 after 48 h. Although hydrogen transfer to C−C triple bonds is quite rare, a report appeared recently describing efficient transfer hydrogenation of alkynes and alkenes with methanol, employing a hydrido(methoxo)iridium(III) complex.[20] C−N multiple bonds are generally more difficult to reduce than C−C and C=O, and relatively few examples are known of their transfer hydrogenation. Successful recent examples of hydrogen transfer to imines employ a formic acid/triethylamine hydrogen donor/base combination.[21] To our knowledge, there are no reports of reduction of C−N triple bonds by homogeneously catalyzed transfer hydrogenation.

Several routes have been proposed in the literature for metal-promoted hydrogen transfer reactions. In Meerwein−Ponndorf−Verley reactions, transfer hydrogenation of ketones with alcohols is promoted by Lewis acidic metal alkoxides[22] via a six-membered cyclic transition state. The currently accepted putative mechanism for late-transition-metal-catalyzed hydrogen transfer involves initial formation of a metal hydride, as shown in Scheme 3.[3,23]

An alternative mechanism has been proposed for metal complexes containing a primary or secondary amine ligand, via a hydrogen-bonded intermediate.[23] The mechanism described in Scheme 3 appears the most likely in our system. The intermediacy of a metal hydride is suggested by the formation of metal hydride (identified by the characteristic high field ^{1}H NMR resonance) on heating a sample of **4** with KOH in 2-propanol, although unfortunately no tractable product was obtained on workup. Since this mechanism requires coordination of the substrate to the metal prior to hydride transfer, the ligand environment plays an important role in the efficacy and selectivity of the process. Ongoing efforts are aimed at understanding the effects of nucleophilic carbenes in catalytic transfer hydrogenation and related homogeneous transformations.

Scheme 3



Conclusion

The replacement of P- and N-donor ligands with nucleophilic carbenes in cationic Ir(I) complexes affords active catalysts in transfer hydrogenation. As previously noted with phosphine ligands, neither steric nor electronic properties alone can account for the different activities observed with the various carbene and diazabutadiene ligands tested. Complex **4** in particular, containing the ICy ligand, is effective in hydrogen transfer reactions with ketones and compares favorably with many of the Ru and cationic Ir(I) complexes previously studied. It also exhibits activity toward hydrogenation of simple olefins, although activation of alkane C−H bonds in the fully saturated products resulted in only monoolefins being obtained from diolefins. No reactivity was observed in hydrogen transfer from 2-propanol to imines and nitriles.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry argon with standard Schlenk tube techniques or in a MBraun glovebox containing less than 1 ppm of oxygen and water. NMR spectra were recorded using Varian 400 or 300 MHz spectrometers. Elemental analyses were performed by Desert Analysis, Tucson, AZ. GC analyses were performed on a Hewlett-Packard HP 5890 II equipped with a FID and a HP-5 column. GCMS analyses were performed on a MicroMass instrument. All reported yields in transfer hydrogenation experiments are GC yields.

Reagents. Substrates for catalysis were purchased from commercial suppliers and either used as received (solid compounds) or degassed prior to use by purging with argon for 20−30 min. Anhydrous ^{i}PrOH and MeOH were purchased from Aldrich, degassed prior to use by purging with argon for 30 min, and then transferred to a Strauss flask equipped with a Teflon stopcock. CH_2Cl_2 was dried by passage through an alumina tower and stored in a glovebox. [Ir(cod)py$_2$]PF_6,[26] IPr, IMes, and ICy·HCl,[24] and DAB-Cy, DAB-Mes, DAB-Ad, and

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DAB-trimethoxyphenyl[25] were prepared according to the literature procedures.

Synthesis of [Ir(cod)(py)(IMes)]PF_6 (2). A 50 mL Schlenk flask was charged with [Ir(cod)py_2]PF_6 (1.0 g, 1.657 mmol), IMes (0.76 g, 2.486 mmol) and toluene (20 mL). The reaction mixture was then stirred at room temperature for 2 days. The yellow precipitate was filtered on a collection frit, washed with hexane, and dried under vacuum to afford a yellow powder. Yield: 1.1 g (82%). Anal. Calcd for $C_{34}H_{41}F_6N_3PIr$: C, 49.27; H, 4.99; N, 5.07. Found: C, 49.31; H, 5.02; N, 5.10. ^{1}H NMR (499.75 MHz, 298 K, CD_2Cl_2): δ 1.62 (br, 4 H, cod CH_2), 1.75−2.25 (br, 16 H, cod CH_2 and Mes *o*-CH_3), 2.42 (s, 6 H, Mes *p*-CH_3), 3.20 (m, 2 H, cod C*H* trans to py), 3.64 (m, 2 H, cod C*H* trans to IMes), 6.99−7.10 (s + br, 6 H, N*H*C=C*H*N + Mes C*H*), 7.16 (m, 2 H, py $H_{3,5}$), 7.71 (tt, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.6 Hz, 1 H, py H_4), 7.76 (dt, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.6 Hz, 2 H, py $H_{2,6}$). ^{1}H NMR (499.75 MHz, 233 K, CD_2Cl_2): δ 1.57 (br, 4 H, cod CH_2), 1.76 (s, 6 H, Mes *o*-CH_3), 1.81, 1.95 (m, 4 H, cod CH_2), 2,24 (s, 6 H, Mes *o*-CH_3), 2.38 (s, 6 H, Mes *p*-CH_3), 3.16 (m, 2 H, cod C*H* trans to py), 3.52 (m, 2 H, cod C*H* trans to IMes), 6.87 (br s, 2 H, Mes C*H*), 7.00 (s, 2 H, N*H*C=C*H*N), 7.11 (br s + m, 4 H, Mes C*H* + py $H_{3,5}$), 7.69 (m, 3 H, py $H_{2,6}$, py H_4). ^{13}C NMR (100.58 MHz, 298 K, CD_2Cl_2): δ 18.65 (s, Mes *C*H_3), 21.42 (s, Mes *C*H_3), 29.81 (s, cod *C*H_2), 33.03 (s, cod *C*H_2), 65.99 (s, cod *C*H), 82.84 (s, cod *C*H), 125.06 (br s, py *C*),125.49 (s, N*C*H=*C*HN), 130.07 (Mes *C*), 135.81 (s, Mes *C*), 137.10 (s, py *C*), 138.00 (s, Mes *C*), 140.56 (s, Mes 1-*C*), 150.97 (s, py *C*), 173.95 (s, N*C*N). Crystals suitable for X-ray measurements were obtained by slow diffusion of ether into a dichloromethane solution of **2**.

Synthesis of [Ir(cod)(py)(IPr)]PF_6 (3). A 50 mL Schlenk flask was charged with [Ir(cod)py_2]PF_6 (500 mg, 0.828 mmol), IPr• (483 mg, 1.24 mmol), and toluene (20 mL). The reaction mixture was then stirred at room temperature for 2 days. The yellow precipitate was filtered on a collection frit, washed with hexane, and dried under vacuum. Yield: 620 mg (82%). Anal. Calcd for $C_{40}H_{53}F_6N_3PIr$: C, 52.62; H, 5.85; N, 4.60. Found: C, 52.80; H, 5.65; N, 4.70. ^{1}H NMR (499.75 MHz, 303 K, CD_2Cl_2): δ 0.8−1.4 (br, ^{i}Pr CH_3), 1.56 (m, 4 H, cod CH_2), 1.87 (m, 2 H, cod CH_2), 1.99 (m, 2 H, cod CH_2), 2.6−3.2 (br, ^{i}Pr C*H*), 3.06 (m, 2 H, cod C*H* trans to py), 3.63 (m, 2 H, cod C*H* trans to IPr), 7.15 (s, 2H, NC*H*=C*H*N), 7.17 (m, 2H, py), 7.2−7.5 (br + m, 5 H, IPr *m*-C*H* + py), 7.5−7.7 (m, 4H, IPr *p*-C*H* + py). ^{1}H NMR (499.75 MHz, 233 K, CD_2Cl_2): δ 0.76 (d, $^3J_{HH}$ = 7 Hz, 6 H, ^{i}Pr CH_3), 0.86 (d, $^3J_{HH}$ = 7 Hz, 6 H, ^{i}Pr CH_3), 1.21 (d, $^3J_{HH}$ = 7 Hz, 6 H, ^{i}Pr CH_3), 1.45 (d, $^3J_{HH}$ = 7 Hz, 6 H, ^{i}Pr CH_3), 1.50 (m, 4 H, cod CH_2), 1.78 (m, 2 H, cod CH_2), 1.94 (m, 2 H, cod CH_2), 2.40 (m, $^3J_{HH}$ = 7 Hz, 2 H, ^{i}Pr C*H*), 2.99 (m, 2 H, cod C*H* trans to py), 3.13 (m, $^3J_{HH}$ = 7 Hz, 2 H, ^{i}Pr C*H*), 3.54 (m, 2 H, cod C*H* trans to IPr), 7.13 (s + m, 4H, NC*H*=C*H*N + py *m*-C*H*), 7.19 (d, 2 H, IPr *m*-C*H*), 7.40−7.42 (br d + t, 3H, IPr *m*-C*H* + py *o*-C*H*) 7.48 (d, 2 H, py *o*-C*H*), 7.59 (t, IPr *p*-C*H*). ^{13}C NMR (100.58 MHz, 298K, CD_2Cl_2): δ 26.15 (s, ^{i}Pr *C*H_3), 29.56 (2, cod *C*H_2), 29.74 (s, ^{i}Pr *C*H), 32.52 (cod *C*H_2), 66.06 (s, cod *C*H), 83.98 (s, cod *C*H), 125.22 (s, Ph *C*H), 125.46 (N*C*H=*C*HN), 126.69 (s, Ph *C*H), 126.75 (s, py *C*), 126.86 (s, Ph *C*H), 131.44 (s, Ph *C*H), 136.34 (s, py *C*), 146.08 (s, Ph *C*H), 150.63 (s, py *C*), 175.56 (s, N*C*N). Crystals suitable for X-ray measurements were obtained by slow diffusion of ether into a dichloromethane solution of **3**.

Synthesis of [Ir(cod)(py)(ICy)]PF_6 (4). In a 50 mL Schlenk flask, a mixture of 250 mg of ICy·HCl (0.930 mmol) and 104 mg of potassium *tert*-butoxide (0.928 mmol) in 10 mL of THF was stirred at room temperature for 4 h. The solvent was then removed completely under vacuum. The residue was extracted with 15 mL of toluene. The brownish solution was filtered and charged with 374 mg of [Ir(cod)py_2]PF_6 (0.619 mmol). The suspension was then stirred at room temperature for 2 days. The orange precipitate was filtered on a collection frit, washed with hexane, and dried under vacuum. Yield: 297 mg (63%). Anal. Calcd for $C_{28}H_{41}F_6IrN_3P$: C, 44.44; H, 5.46; N, 5.50. Found: C, 44.54; H, 5.36; N, 5.70. ^{1}H NMR (399.95 MHz, 298 K, CD_2Cl_2): δ 1.26−2.46 (m, 28 H, Cy CH_2), 3.87 (s, 2 H, cod C*H*), 3.93 (s, 2 H, cod C*H*), 4.67 (m, 2 H, Cy 1-C*H*), 7.10 (s, 2 H, NC*HC*H), 7.49 (m, 2 H, py), 7.80 (m, 1 H, py), 8.62 (m, 2 H, py). ^{13}C NMR (75.43 MHz, 298 K, CD_2Cl_2): δ 25.51, 25.64, 25.91, 26.19, 26.4, 26.59 (all s, Cy *C*), 32.80 (s, cod *C*H_2), 34.38 (s, cod *C*H_2), 61.57 (s, Cy 1-*C*), 64.67 (s, cod *C*H), 74.79 (s, cod *C*H), 119.40 (N*C*H=*C*HN), 127.33 (s, py-*C*), 139.05 (s, py *C*), 150.44 (s, py *C*), 174.87 (s, N*C*N). Crystals suitable for X-ray measurements were obtained by slow diffusion of ether into a dichloromethane solution of **4**.

Catalytic Reactions. A 0.02 mmol portion of catalyst (0.01 mmol of **4** for all reactions described in Table 6) and 0.2 mmol of potassium hydroxide were loaded into either a Schlenk tube or a scintillation vial fitted with a TFE/silicone liner and a screw cap inside a glovebox. After removal from the glovebox, 2-propanol (20 mL) was added by syringe and the resulting yellow solution heated at 80 °C for 30 min under argon. In reactions where the catalyst was prepared in situ, a solution of 0.02 mmol of [Ir(cod)$(py)_2$]PF_6, 0.02 mmol of ligand, and 0.2 mmol of potassium hydroxide in 20 mL of 2-propanol was loaded into a Schlenk tube fitted with a septum inside a glovebox. The resulting solution was heated at 80 °C for 30 min under argon. Following injection of 4 mmol of substrate the reaction mixture was stirred at 80 °C and the product ratio monitored by GC analysis. Products were identified either by comparison of GC retention times with those of authentic samples or by GCMS.

X-ray Diffraction Measurements. Single crystals of **2**−**4** were obtained by diffusion of diethyl ether into a solution of the complex in CH_2Cl_2. A single crystal was placed in a capillary tube and mounted on a Bruker SMART CCD X-ray diffractometer. Data were collected using Mo Kα radiation at 170 K (**2** and **3**) or 150 K (**4**). The structures were solved using direct methods (SHELXS-86) and refined by full-matrix least-squares techniques. Crystallographic data can be found in Table 2 and selected bond distances and angles in Table 3.

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Supporting Information Available: Tables giving details of the crystal structure determination and crystallographic data for **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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