Chelated Iridium(III) Bis-carbene Complexes as Air-Stable Catalysts for Transfer Hydrogenation

Martin Albrecht, John R. Miecznikowski, Amanda Samuel, Jack W. Faller,* and Robert H. Crabtree*

Department of Chemistry, Yale University, 225 Prospect Street, New Haven, Connecticut 06520

Received April 29, 2002

The new air-stable and moisture-insensitive Ir catalysts for efficient transfer hydrogenation of ketones contain a chelating bis(N-heterocyclic carbene) ligand. Most other hydrogen transfer catalysts show activity Rh > Ir, but we find Ir > Rh for these cases. Tuning of the ligand wingtip substituents, R, can greatly increase catalyst activity (R = neopentyl) or selectivity (R = isopropyl). Reactivity studies and isotopic labeling are consistent with a monohydride mechanism for the hydrogen transfer.

Introduction

Arduengo-type carbenes have been attracting great attention recently as ligands for homogeneous catalysis,[1] where they are sometimes considered phosphine analogues. To date, monodentate systems have generally been studied, but only very rarely the carbene analogues of chelating diphosphines.[2] This is probably because few synthetic routes are known to be transferable from the monodentate case. For example, deprotonation conditions using strong bases such as NaH or BuLi, often required to convert the precursor imidazolium salt to the free carbene, could possibly (although not necessarily[1e]) attack $-CH_2-$ linkers between the carbene units or other sensitive sites. Chelate carbenes could be very useful, however, since stability would likely be improved, for example by slowing decomposition reactions, such as reductive elimination of the carbene. The rare known routes to chelating bis-carbene complexes[3] have so far been predominantly applied to Pd, including some cases from our group.[4] Peris and coworkers first synthesized the Rh species [Rh(III)(bis-carbene)(OAc)I_2], which were subsequently studied for catalysis.[5] With Ir and Rh another synthetic problem became apparent: the deprotonation route has previously given only bimetallic species, in which each carbene moiety coordinates to a different metal center.[6,7] Our route,[5] relying instead on metalation by Rh salts with OAc^- as mild base and I^- as ligand, gave true chelates. We now report an extension of the direct metalation protocol to give the analoguous chelating iridium(III) complexes. The Ir(bis-carbene) complexes so obtained show even better activity as hydrogen transfer catalysts,[8] and the activity and selectivity can be tuned by simple ligand modifications. Unlike their phosphine analogues, chelating carbene complexes tend to be air and water stable. This proves to be the case here: even the catalytic reaction itself can be carried out without a blanket of inert gas or special reagent purification or need for dry solvents. Beyond the added convenience, this may allow broader practical application.

Results and Discussion

Synthesis of Ligands and Iridium(III) Complexes. A series of bis-imidazolium salts (**1a**−**f**, Scheme 1) have been prepared as ligand precursors by condensation of readily accessible, substituted alkyl imidazole

(1) (a) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. I.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530. (b) Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185. (c) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162. (d) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (e) Arduengo, A. J., III. Personal communication.

(2) For *C, N*-bidentate coordinating carbene chelates, see: (a) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741. (b) Powell, M. T.; Hou, D.-R.; Perry, M. C.; Cui, X.; Burgess, K. *J. Am. Chem. Soc.* **2001**, *123*, 8878. (c) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *Chem. Commun.* **2001**, 2274.

(3) For first-row transition metal complexes containing chelating carbenes, see: (a) Öfele, K.; Herrmann, W. A.; Mihalios, D.; Elison, M.; Herdtweck, E.; Priermeier, T.; Kiprof, P. *J. Organomet. Chem.* **1995**, *498*, 1. (b) Kernbach, U.; Ramm, M.; Luger, P.; Fehlhammer, W. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 310. (c) Fränkel, R.; Kernbach, U.; Bakola-Christianopoulou, M.; Plaia, U.; Suter, M.; Ponikwar, W.; Nöth, H.; Moinet, C.; Fehlhammer, W. P. *J. Organomet. Chem.* **2001**, *617*−*618*, 530. (d) Douthwaite, R. E.; Haussinger, D.; Green, M. L. H.; Silcock, P. J.; Gomes, P. T.; Martins, A. M.; Danopoulos, A. A. *Organometallics* **1999**, *18*, 4584.

(4) (a) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371. (b) Fehlhammer, W. P.; Bliss, Kernbach, U.; Brüdgam, I. *J. Organomet. Chem.* **1995**, *490*, 149. (c) Clyne, D. S.; Jin, J.; Genest, E.; Gallucci, J. C.; RajanBabu, T. V. *Org. Lett.* **2000**, *2*, 1125. (d) Tulloch, A. A. D.; Danopoulos, A. A.; Tizzard, G. J.; Coles, S. J.; Hursthouse, M. B.; Hay-Motherwell, R. S.; Motherwell, W. B. *Chem. Commun.* **2001**, 1270. (e) Baker, M. V.; Skelton, B. W.; White, A. H.; Williams, C. C. *J. Chem. Soc., Dalton Trans.* **2001**, 111. (f) Gründemann, S.; Albrecht, M.; Loch, J. A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2001**, *20*, 5485. (g) Loch, J. A.; Albrecht, M.; Mata, J.; Peris, E.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 700.

(5) Albrecht, M.; Crabtree, R. H.; Mata, J.; Peris, E. *Chem. Commun.* **2002**, 32.

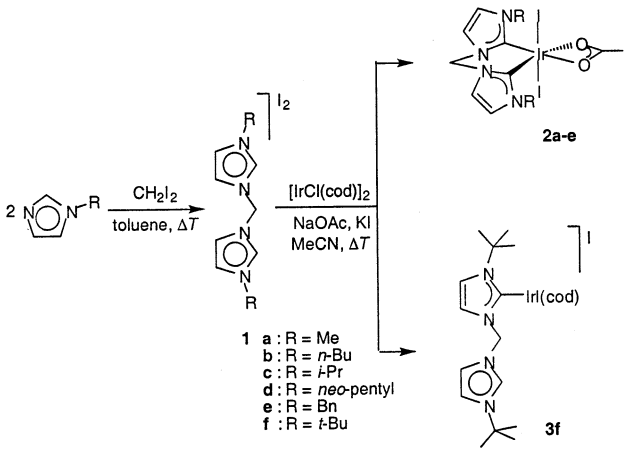
(6) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Chem. Eur. J.* **1996**, *2*, 772.

(7) Rh(I) bis-carbene complexes have been prepared from electron-rich olefins, see: (a) Hitchcock, P. B.; Lappert, M. F.; Terreros, P.; Wainwright, K. P. *J. Chem. Soc., Chem. Commun.* **1980**, 1180. (b) Shi, Z.; Thummel, R. P. *Tetrahedron Lett.* **1995**, *36*, 2741.

(8) (a) Linn, D. E.; Halpern, G. *J. Am. Chem. Soc.* **1987**, *109*, 2969. (b) Zassinovich, G.; Mestroni, G.; Gladiali, S. *Chem. Rev.* **1992**, *92*, 1051. (c) Gladiali, S.; Mestroni, G. In *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 2, pp 97−119. (d) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97.

10.1021/om020338x CCC: $22.00
Publication on Web 07/25/2002

Scheme 1. Synthesis of the Iridium Bis-carbene Complexes 2



with diiodomethane in nonpolar solvents.[9] Metalation of these bis-imidazolium salts with the metal precursor $[IrCl(cod)]_2$ occurs readily in the presence of KI and NaOAc on heating (MeCN, reflux; Scheme 1). Both the reaction itself and the final iridium carbene complexes **2** are insensitive to air and moisture both in the solid state and in solution. No exclusion of air is necessary at any stage, and the reaction proceeds in modest to good yields whether the solvents are dried or air is excluded. The products were typically purified by column chromatography on SiO_2, which did not decompose the products. All the iridium(bis-carbene) complexes are very soluble in chlorinated solvents, acetone, and thf, but are virtually insoluble in hydrocarbon solvents and Et_2O.

Metalation occurred with concomitant two-electron oxidation to iridium(III) in all cases, except for ligand **1f**, with bulky *t*Bu peripheral substituents, which gave the iridium(I) complex **3f** as the only isolable product under identical reaction conditions. Neither prolonged reaction times nor addition of a base (K_2CO_3, NaOAc, KO*t*Bu) promoted a second C−H bond activation in **3f** with formation of the chelated bis-carbene **2f**.

Spectroscopy. The chelating character of the bis-carbene ligand can be deduced from NMR spectroscopy by analogy with the spectra of the crystallographically characterized Rh analogues.[5] In complexes **2**, only one set of signals has been detected for the protons of the carbene chelate, indicating that the two halves are symmetry-related. The two heterocyclic protons appear in the aromatic region as two doublets with the expected small coupling constants ($^3J_{HH}$ typically 2 Hz; $CDCl_3$ solution). The singlet multiplicity of the resonances assigned to the methylene group linking the two heterocycles around δ 6.6 illustrates a fluxional rather than a locked conformation of the chelate metallacycle. Such a behavior has been established previously in similar cases.[3a,10] Most characteristically, the $^{13}C\{^1H\}$ spectrum shows a low-field singlet at δ 127 for the iridium-bound carbon. The acetate anion gives rise to the appropriate NMR signals (δ_H 1.9, δ_C 190 and 31).

(9) Williams, D. J.; Vanderveer, D.; Jones, R. L.; Menaldino, D. S. *Inorg. Chim. Acta* **1989**, *165*, 173.

(10) (a) Gardiner, M. G.; Herrmann, A. W.; Reisinger, C.-P.; Schwarz, J.; Spiegler, M. *J. Organomet. Chem.* **1999**, *572*, 239. (b) Douthwaite, R. E.; Hauessinger, D.; Green, M. L. H.; Silcock, P. J.; Gomes, P. T.; Martins, A. M.; Danopoulos, A. A. *Organometallics* **1999**, *18*, 4584.

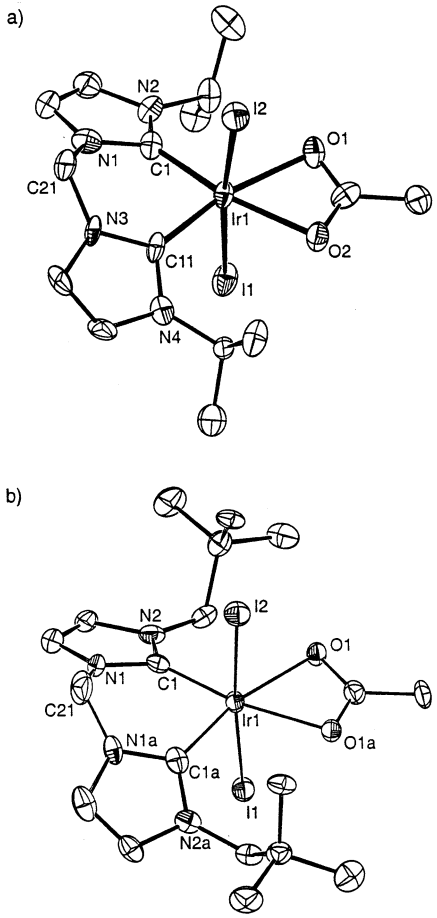


Figure 1. Perspective view (50% probability) of the molecular structures of iridium(III) complexes **2c** (a) and **2d** (b); hydrogen atoms are omitted.

The iridium(I) complex **3f**, having a monodentate carbene ligand and a pendant imidazolium group, shows different sets of NMR resonances for each heterocycle, including a low-field signal at δ 10.44 assigned to the acidic NCHN proton of the imidazolium group ($CDCl_3$ solution). The low symmetry causes the resonances for the methylene linker to appear as two AB doublets (δ 7.80 and 7.41, respectively, $^2J_{HH}$ = 12.9 Hz). This suggests that the coordinated carbene is oriented out of the square plane of the complex and that M−C bond rotation is slow on the NMR time scale. By disfavoring reactive conformations, this rigidity could be a factor in preventing **3f** from going on to the chelate form **2f**. Additional NMR data confirm the structure. The metal-bound carbene carbon resonates at markedly lower field than in the chelating bis-carbene complexes (δ_{C-Ir} 180.52, compared to δ_{C-Ir} 127 in **2a**−**d**). All data are consistent with the proposed structure **3f** (Scheme 1). Because the desired chelation was not achieved, we did not look at the properties of the monocarbene complex **3f** in any detail; they may be very similar to those of the related iridium(I) carbene complexes.[11]

Structures of 2c and 2d. Unambiguous evidence for the proposed structures of **2** was obtained by X-ray diffraction analyses. The structures of **2c** and **2d** in Figure 1 show common features. For example, the pertinent bond angles and distances around iridium

(11) Hillier, A. C.; Lee, H. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 4246.

Table 1. Selected Bond Lengths and Angles in Complexes 2c and 2d[a]

	2c	**2d** (C11 = C1a)
	Bond Lengths (Å)	
Ir1−C1	1.965(13)	1.984(8)
Ir1−C11	1.981(12)	
Ir1−I1	2.6739(10)	2.6783(10)
Ir1−I2	2.6667(10)	2.6825(11)
Ir1−O1	2.181(8)	2.173(6)
Ir1−O2	2.187(8)	
	Bond Angles (deg)	
C1−Ir1−C11	86.4(5)	87.2(3)
C1−Ir1−I1	91.1(4)	90.6(2)
C11−Ir1−I1	91.3(3)	
C1−Ir1−I2	95.5(4)	92.9(2)
C11−Ir1−I2	90.7(3)	
C1−Ir1−O1	106.8(5)	106.4(3)
C11−Ir1−O1	166.8(4)	166.1(3)
C1−Ir1−O2	167.2(4)	
C11−Ir1−O2	106.4(4)	
I1−Ir1−I2	173.19(3)	175.25(3)
O1−Ir1−O2	60.5(3)	59.8(2)
	Torsion Angles (deg)	
C11−Ir1−C1−N1	19.5(10)	21.6(7)
O1−Ir1−C1−N2	22.9(11)	24.7(8)

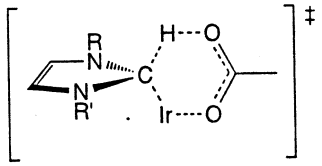


Figure 2. Proposed transition state for the acetate-mediated metalation of imidazolium salts.

are identical within their esd's, indicating that the peripheral isopropyl and neopentyl substituents have no significant stereoelectronic effects on the metal center. The symmetry deduced from solution spectroscopy are reflected in the crystal structures, and in **2d**, the molecule is located on a plane of symmetry that relates the two heterocyclic rings crystallographically. In both structures, the geometry is distorted octahedral, with *trans* iodides and bidentate coordinating acetate and bis-carbene ligands. The carbene's bite angle C1−Ir1−C11 of 87° is very appropriate for octahedral coordination, but the ligand is buckled so that the heterocycles deviate from the coordination plane by ca. 20°. The peripheral alkyls shield the same side of the iridium coordination sphere and give rather close contacts between the acetate oxygen and an α-proton of the alkyl (**2c**: C−H···OAc is 2.323 and 2.334 Å, respectively; **2d**: C−H···OAc is 2.415 Å). These results support the idea that a sterically demanding substituent such as *t*Bu could prevent carbene chelation.

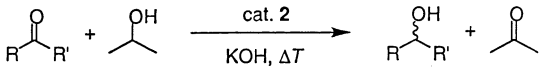
Metalation. The oxidant that leads to formation of Ir(III) has not been identified: H_2 may be evolved. There is no metallic mirror, so disproportionation to Ir(0) is excluded. Product yields are similar in air or under Ar, so O_2 does not seem to be the oxidant, although it is difficult to exclude the participation of traces of air. The metalation mechanism is uncertain but, in the absence of strong bases, may require stepwise C−H bond activation, in which **3f** could be an intermediate. Since acetate seems especially useful as a base, a possible path involves a cyclic TS (Figure 2); this would also explain the viability of carbonate as an alternative base for the palladation of imidazolium salts.[12]

Table 2. Influence of Wingtips on the Catalytic Activity of Ir(bis-carbene) Complexes[a]

entry	catalyst	catalyst R group	time/min [b]	TOF_{50}/h^{-1} [c]
1	**2a**	Me	90	2000
2	**2b**	*n*Bu	90	2000
3	**2c**	*i*Pr	120	1000
4	**2d**	neopentyl	4	50 000
5	**2e**	benzyl	>1200	<10

[a] Transfer hydrogenation of benzophenone, reaction conditions: S/C/base 1000:1:5 with 0.2 M substrate in 10 mL of *i*PrOH at reflux temperature. [b] Reaction time required for conversions >98%. [c] Turnover frequency at 50% conversion.

Catalytic Transfer Hydrogenation. The iridium(bis-carbene) complexes **2** catalyze the reduction of ketones to the corresponding alcohols via hydrogen transfer from *i*PrOH with KOH as the promoter (eq 1). In contrast to our previously reported rhodium(III) bis-carbene complexes, which required concentrated base,[5] the iridium(III) analogues are already efficient catalysts at moderate base concentrations with a typical catalyst/base ratio of 0.2. Removal of the dehydrogenated donor species (acetone in most cases) was not necessary to complete the reaction and did not influence the rate significantly. Clearly the excess *i*PrOH drives the reaction by mass action.



(1)

S/C/base 1000/1/5

We have screened the performance of the Ir(bis-carbene) catalysts in transfer hydrogenation by using benzophenone as a representative substrate and substrate/catalyst/base (S/C/base) ratios of 1000:1:5. The results, in Table 2, show the influence of the nature of R on catalyst activity. Catalysts containing primary alkyls (R = Me, *n*Bu, neopentyl) are more active than ones with secondary alkyl (R = *i*Pr in **2c**, entry 3). By far the most efficient catalyst is the neopentyl complex **2d** (entry 4), which transfer hydrogenates benzophenone to >98% conversion in only 4 min with a turnover frequency at 50% conversion of 50 000 h^{-1}. This activity is significantly higher than for related iridium(I) monocarbene complexes[11] and compares well with the most active transfer hydrogenation catalysts previously described.[13] Since the different peripheral substituents of the bis-carbene ligands seem to have little electronic influence on the metal center or on the bite angle of the bis-carbene ligand (cf. X-ray analysis, Figure 1), steric effects may possibly help to account for the remarkably high activity of **2d**.

(12) For examples, see: (a) Herrmann, W. A.; Schwarz, J.; Gardiner, M. G. *Organometallics* **1999**, *18*, 4082. (b) Zhang, C.; Huang, J.; Trudell, M. L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804. (c) Chen, J. C. C.; Lin, I. J. B. *J. Chem. Soc., Dalton Trans.* **2000**, 839. (d) Tulloch, A. A. D.; Danopoulos, A. A.; Winston, S.; Kleinhenz, S.; Eastham, G. *J. Chem. Soc., Dalton Trans.* **2000**, 4499.

(13) For catalysts exhibiting high TON or TOF, see: (a) Mestroni, G.; Zassinovich, G.; Camus, A.; Martinelli, F. *J. Organomet. Chem.* **1980**, *198*, 87. (b) Nordin, S. J. M.; Roth, P.; Tarnai, T.; Alonso, D. A.; Brandt, P.; Andersson, P. G. *Chem. Eur. J.* **2001**, *7*, 1431. (c) Dani, P.; Karlen, T.; Gossage, R. A.; Gladiali, S.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 743.

Table 3. Screening Conditions for Catalytic Transfer Hydrogenation of Acetophenone[a]

entry	catalyst (mol %)	solvent/base	time/h	temp/°C	yield/%	TON
1		*i*PrOH/KOH	24	82	<5	
2	**2c** (1)	*i*PrOH/KOH	0.2	82	>98	100
3	**2c** (0.1)	*i*PrOH/KOH	2	82	>98	1000
4	**2c** (0.01)	*i*PrOH/KOH [b]	24	82	39	3900
5	**2d** (0.01)	*i*PrOH/KOH [b]	24	82	53	5300
6	**2c** (0.1)	*i*PrOH/KOH	2	70	>98	1000
7	**2d** (0.1)	*i*PrOH/KOH	24	25	>98	1000
8	**2c** (0.1)	*i*PrOH [c]	24	82	<5	
9	**2c** (0.1)	$HCOOH/NEt_3$ [d]	24	25	<5	
10	**2c** (0.1)	MeOH/KOH	24	65	<5	
11	**2c** (0.1)	cyclohexanol/KOH	4	100	>98	1000

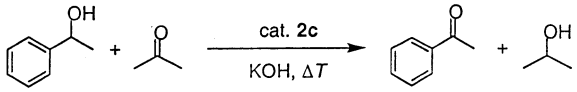
[a] Reaction conditions: 0.2 M substrate solutions, molar ratio catalyst/base 1:5, unless stated otherwise. Product yields determined by ^{1}H NMR. [b] Catalyst/base 1:10. [c] No base added, catalyst was stirred in *i*PrOH at reflux for 30 min before adding substrate. [d] Azeotropic mixture ($HCOOH/NEt_3$, 5:2).

Catalyst deactivation could occur via Hofmann elimination of the peripheral substituent[14] and subsequent metal decoordination, although we did not detect any elimination products. Complex **2d**, containing neopentyl substituents, is expected to be resistant toward this elimination, since β-hydrogens are absent. However, benzylic groups that also lack β-hydrogens give virtually no catalytic activity in the case of **2e**.

Optimization of Reaction Conditions. At substrate/catalyst ratio S/C 1000, good conversion rates are generally observed with all Ir(bis-carbene) systems. Higher catalyst loading obviously accelerates the hydrogen transfer and even with the slower systems (R = *i*Pr) gives complete hydrogenation of acetophenone within less than 30 min (Table 3, entries 1−3). Further lowering of the catalyst loading is unattractive: at S/C 10 000, conversion does not exceed 39% for **2c** (entry 4) and 53% for **2d** (entry 5). Moreover, significantly longer reaction times are required (24 h compared to minutes for complete reduction with S/**2d** 1000). The influence of the base concentration on the catalytic activity becomes particularly pronounced at such low catalyst loading. Using Ir/KOH ratios of 1:5 typically gave less than 10% transfer hydrogenation after 24 h. Finally, catalytic reactions at ambient temperature (RT, entry 7) gave complete, yet slow hydrogen transfer.

Modification of the solvent/base system had dramatic effects (entries 8−11). In the absence of an external base, no reaction was observed. Apparently, the coordinated acetate ion is not basic enough to deprotonate *i*PrOH. This suggests that a different mechanism operates than the concerted proton−hydride transfer proposed for many Ru(amino alcohol) systems.[8d,15] Cyclohexanol was a less efficient but still satisfactory hydrogen donor system, but no reaction was observed in MeOH. The complexes were inactive with a formic acid−triethylamine azeotrope, although this system can be a valuable alternative for transfer hydrogenation at ambient temperatures.[16]

Attempted Oxidation. Since transfer hydrogenation is potentially reversible, product oxidation back to the original substrate is possible, though usually undesirable especially in asymmetric synthesis. In an attempt to reverse the direction of the hydrogen transfer, catalytic oxidation of phenethyl alcohol to acetophenone has been probed with the iridium(III) catalyst **2c** (eq 2).



(2)

Oxidation is significantly slower than the corresponding reduction of acetophenone, and under comparable reaction conditions (S/C/base 1000:1:5, acetone as solvent and hydrogen acceptor), only 12% conversion is observed after 2 h, the reaction time required for complete reduction of acetophenone. At higher base strength (S/C/base 1000:1:10) or with higher catalyst loading (S/C/base 200:1:5), up to 60% conversion to acetophenone has been observed. Cyclohexanone was an inadequate acceptor, and no hydrogen transfer was seen (cf. 4 h reaction time for the reverse reaction, Table 3, entry 11).

Table 4. Compatibility with Functional Groups[a]

entry	catalyst (mol %)	substrate	time/h	yield/%	TON
1	**2c**	4-bromoacetophenone	2	>98	1000
2	**2c**	4-nitroacetophenone	2	>98	1000
3	**2c**	4-acetyl-*trans*-stilbene	(2) 24	(42) 76	760
4	**2c**	4-methoxy acetophenone	(2) 20	(48) 80	800
5	**2d**	4-methoxy acetophenone	(1) 2	(79) 83	830
6	**2c**	2-acetylpyridine	15	19	190
7	**2c**	4-acetylpyridine	18	13	130
8	**2c**	acetophenone, pyridine	20	24	240
9	**2c**[b]	benzylidene methylimine	20	<10	
10	**2c**[b]	3,5-dimethyl benzonitrile	8	<5	

[a] Reaction conditions: S/C/base 1000:1:5 with 0.2 M substrate in 10 mL of *i*PrOH at reflux temperature, unless stated otherwise. Yields determined by ^{1}H NMR. [b] S/C/base, 200:1:5.

Tolerance of Functional Groups. A variety of functionalized acetophenones were monitored (Table 4). Aromatic bromo and nitro substituents do not have a significant effect on the rate of hydrogen transfer (entries 1 and 2). More importantly, none of these groups are affected during catalysis and no indication of either NO_2 to NH_2 reduction or dehalogenation was observed.[17] Apparently, oxidative addition of aryl halides Ar−X and competitive reductive elimination of Ar−H and Ar−X is slow, possibly owing to the high oxidation state of the catalyst. Styrene- and more specially MeO-substituted acetophenones are hydrogenated considerably slower (entries 3−5), and complete hydrogen transfer required higher catalyst loading rather than longer reaction times. Extended reaction times do not change yields significantly.

Pyridyl ketones are not hydrogenated efficiently (entries 6 and 7), possibly because 2-acetylpyridine or its reduced hydroxyl analogue could inhibit catalysis as a *N*,*O*-bidentate chelating ligand, especially under the

(14) (a) Horváth, A. *Synthesis* **1994**, 102. (b) Tumelty, D.; Cao, K.; Holmes, C. P. *Org. Lett.* **2001**, *3*, 83.

(15) (a) Haack, K.-J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 285. (b) Alonso, D. A.; Brandt, P.; Nordin, S. J. M.; Andersson, P. G. *J. Am. Chem. Soc.* **1999**, *121*, 9580.

(16) (a) Brunner, H.; Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1180. (b) Brown, J. M.; Brunner, H.; Leitner, W.; Rose, M. *Tetrahedron: Asymmetry* **1991**, *2*, 331. (c) Fujii, A.; Hashiguchi, S.; Uematsu, N.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 2521.

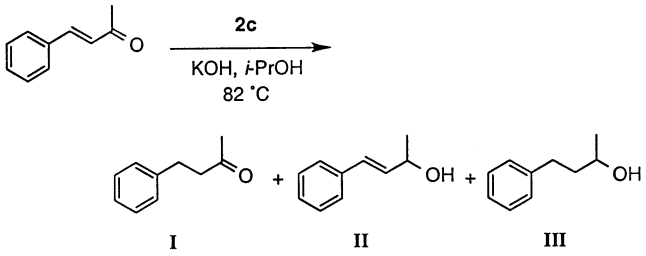
(17) (a) Bressan, M.; d'Alessandro, N.; Liberatore, L.; Morvillo, A. *Coord. Chem. Rev.* **1999**, *185−186*, 385. (b) Inoue, S.; Nomura, K.; Hashiguchi, S.; Noyori, R.; Izawa, Y. *Chem. Lett.* **1997**, 957.

Table 5. Influence of Steric Modifications in Ligand and Substrates[a]

entry	catalyst (mol %)	substrate	time/h	yield/%	TON
1	**2c** (0.1)	acetophenone	2	>98	1000
2	**2d** (0.1)	acetophenone	0.07	>98	1000
3	**2c** (0.1)	cyclohexanone	0.25	>98	1000
4	**2d** (0.1)	cyclohexanone	0.07	>98	1000
5	**2b** (0.1)	2-hexanone	(2) 24	(77) 88	880
6	**2c** (0.1)	2-hexanone	(2) 24	(91) >98	1000
7	**2d** (0.1)	2-hexanone	(0.5) 24	(42) 93	930
8	**2c** (0.1)	3-hexanone	(2) 24	(30) 45	450
9	**2d** (0.1)	3-hexanone	(0.25) 24	(26) 84	840
10	**2c** (0.1)	2-naphthaldehyde	1	>98	1000

[a] Reaction conditions: S/C/base 1000:1:5 with 0.2 M substrate in 10 mL of *i*PrOH at reflux temperature, unless stated otherwise. Yields determined by ^{1}H NMR or GC. [b] At 25 °C.

Table 6. Catalytic Transfer Hydrogenation of α,β-unsaturated Ketone[a]



			yield/%			
entry	catalyst (mol %)	time/h	I	II	III	TON
1	**2c** (0.1)	20	62	18	12	1040
2	**2c** (0.5)	4	0	0	>98	400
3	**2d** (0.1)	20	56	8	<2	640
4	**2d** (0.5)	7	16	0	84	368

[a] Reaction conditions: C/base 1:5 with 0.2 M substrate in 10 mL of *i*PrOH at reflux temperature.

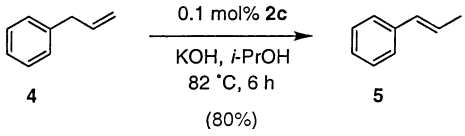
highly basic conditions. Attempted hydrogenation of potentially nonchelating 4-acetylpyridine was similarly unsuccessful, however, so the pyridyl nitrogen may be a poison. Independent runs using acetophenone with 0.5 mol equiv pyridine support this conclusion, and the observed conversion rates were significantly lower (entry 8). We assume that substrate binding is strongly inhibited by the amine. It is therefore no surprise that reduction of *N*-methylbenzylimine to the corresponding amine is not effective (entry 9).

The steric selectivity of the iridium(bis-carbene) catalysts **2** is noteworthy. Ketones containing two small substituents (Ph, Me) are reduced slightly slower than substituents with constrained geometries (cyclohexanone, Table 5, entries 1−4). With ketones containing a larger substituent such as a *n*-butyl group in 2-hexanone, the hydrogen transfer rate drops sharply and days rather than hours are required to ensure complete substrate reduction (entries 5−7). The effect becomes even more pronounced when both ketone substituents are sterically demanding, such as in 3-hexanone (entries 8 and 9). Complex **2c** fails to catalyze the hydrogen transfer in significant yields with such bulky ketones. Hence, these catalyst systems might be useful candidates for selective reductions, e.g., with more complicated substrate molecules that contain several ketone moieties in different steric environments. Competition experiments with 3-hexanone and acetophenone gave predominant consumption of the latter (70% after 2 h), while hexanone reduction was comparably slow (14%).

If the bis-carbene ligand provides a size-selective coordination pocket that excludes bulky substrates, sterically demanding R groups (isopropyl groups in **2c**) should enhance the effect. Accordingly, the reduction of naphthaldehyde, bearing the smallest substituent, is relatively fast (entry 10) and does not lead to self-condensation products.[18] Remarkably, tolylaldehyde is not reduced under the applied catalytic conditions and inhibits the reduction, since its presence fully suppresses the hydrogenation of naphthaldehyde.

With α,β-unsaturated ketones as substrates, the carbonyl and the olefin moiety are both reduced, although higher catalyst loadings were required to ensure complete ketone reduction (Table 5). Sampling reveals that anones resulting from C=C bond reduction are the major intermediates, while enol type compounds from C=O hydrogenation are detected in minor quantities only. This suggests that reduction of the activated double bond is preferred to C=O reduction, which is in agreement with the general trends seen in hydrogen transfer catalysis.[8c] Remote conjugated C=C double bonds such as in 4-acetylstilbene are not affected, however (Table 4, entry 3). Carvone, a sterically demanding cyclohexenone derivative, is not substantially reduced, either at the conjugated C=C bond or at the ketone site and irrespective of the type of iridium(III) catalyst used. This could be explained if the size-selective coordination pocket of the iridium(bis-carbene) catalyst excludes carvone as a substrate.

The results from the transfer hydrogenation to α,β-unsaturated ketones suggested that the iridium(bis-carbene) complexes **2** can also catalyze intramolecular hydrogen transfer reactions such as double-bond migration. This has been verified by using allylbenzene **4** as substrate under conditions identical to those used for the transfer hydrogenation of ketones (refluxing *i*PrOH, KOH; eq 3). After 6 h, β-methylstyrene **5** was observed as the major product (80%; >90% after 18 h), together with starting material. Similar results were obtained with cyclic alkene substrates, and 1,5-cyclooctadiene gradually isomerized into the 1,4- and 1,3-diene. Neither with allylbenzene nor with any diene substrate was saturation resulting from C=C bond hydrogenation seen.



(3)

A significant advantage of these catalysts is their insensitivity toward air and moisture, in contrast to what is observed for most other transfer hydrogenation catalysts. In this way, laborious manipulations and extensive pretreatment of solvents and substrates is avoided. Moreover, monitoring of the reaction progress is very convenient. With benzophenone as substrate, for example, we already observed significant product formation after 4 min (91% conversion at a 0.1 mol %

(18) (a) Ito, T.; Horino, H.; Koshiro, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 504. (b) Menashe, N.; Shvo, Y. *Organometallics* **1991**, *10*, 3885.

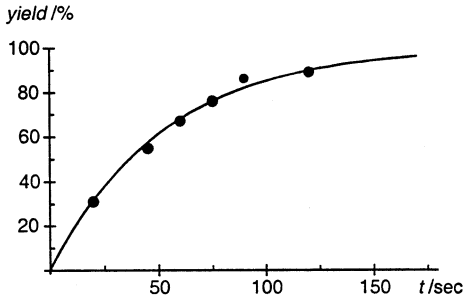


Figure 3. Time dependence of the transfer hydrogenation of benzophenone using 0.1 mol % **2d** as catalyst in *i*PrOH. The solid line corresponds to a pseudo-first-order fit with $k = 19.5 \pm 0.8$ ms^{-1}.

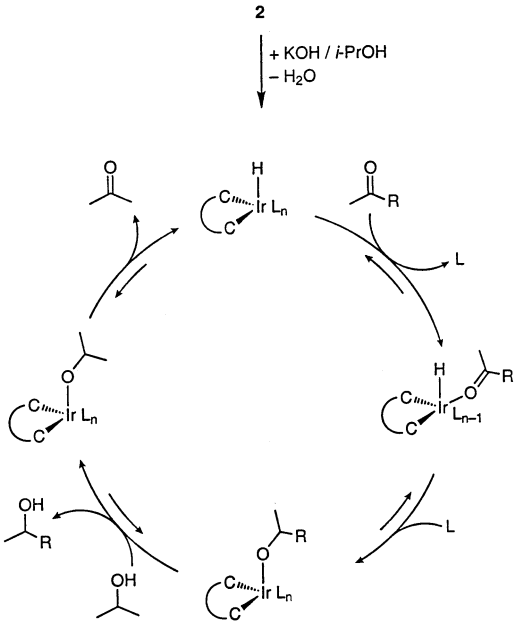
loading of **2d**), but after 2 min, only 17% conversion was observed. This reduced activity in the very initial stage of the reaction is probably caused by the low catalyst activity at reduced temperatures rather than an induction period because when a substrate/*i*PrOH solution is preheated to 80 °C before catalyst and base are added, a conversion of 67% is observed after 1 min, and after 4 min, the reaction is essentially complete (Figure 3). On the basis of these measurements, a pseudo-first-order rate constant $k = 19.5 \pm 0.8$ ms^{-1} has been deduced for the **2d**-catalyzed hydrogen transfer, which corresponds to a turnover frequency at 50% conversion of $TOF_{50} = 50\,000$ h^{-1}. Apparently, the preactivation for the iridium(bis-carbene) catalyst precursors is completed in seconds.

Catalyst Deactivation. Prolonged incubation of the Ir(bis-carbene) catalyst in *i*PrOH in the presence of KOH at reflux temperature in the absence of substrate gave a reaction mixture that is virtually inactive in transfer hydrogenation. For example after a 4 h incubation period of **2c**, less than 5% acetophenone was subsequently reduced within 2 h (cf. >98% hydrogenation without prior incubation). No deactivation is observed, however, when **2c** is preheated in the absence of KOH. Obviously, gradual decomposition of the catalytically active species occurs under strongly basic conditions unless protected by substrate, and it is important to choose a catalyst loading that promotes full conversion within a reasonable time period.

Attempted Recycling of 2. In line with the idea of substrate protection, the catalysts could not be efficiently recycled. Catalytic runs were carried using **2d** as the catalyst and 2-hexanone as the substrate. Both the substrate and the corresponding product 2-hexanol were removed together with the solvent after 2 h of transfer hydrogenation. Using the yellow residue so obtained for a second catalytic run with acetophenone as the new substrate, 53% conversion was detected after 4 h. Seeing that acetophenone is completely hydrogenated in only 4 min in the first run (cf. Table 5, entry 2), the drop in activity is significant (>100 fold). This shows that these complexes are clearly not attractive for recycling. Attempts to regenerate the catalyst by an aqueous workup, i.e., including removal of residual KOH, likewise gave catalytically inactive material.

Mechanism. Classical organic transfer hydrogenation catalysts, e.g., [Al(O*i*Pr)$_3$] in the MeerweinPonndorf-Verley (MPV) reduction, are assumed to involve a metal-templated, direct hydride transfer from the carbinol to the substrate. Direct hydrogen transfer is typically

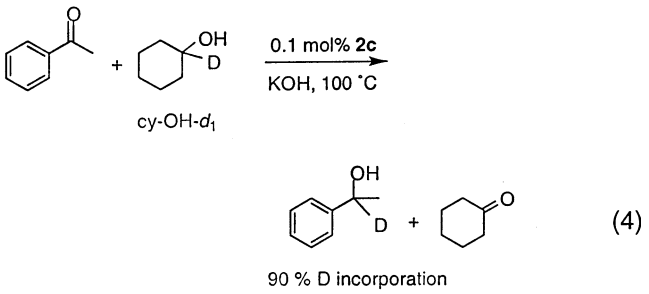
Scheme 2. Proposed Schematic Catalytic Cycle for the Hydrogen Transfer Catalyzed by Iridium(bis-carbene) Complexes Involving a Monohydride Active Species



catalyzed by main group metals and involves a six-membered transition state as a key structure. On the other hand, transition metal-catalyzed hydrogen transfer is supposed to follow the "hydridic route", involving either a monohydride or a dihydride species in the catalytic cycle.[8b] In our efforts to distinguish between these two possibilities, we adapted a labeling protocol previously developed by Pàmies and Bäckvall.[19] On the basis of the fact that hydrogen transfer in the monohydride pathway proceeds through a well-defined intermediate and therefore is specific, they proposed that a deuterium bound to the carbionol carbon must be transferred to the carbonyl carbon exclusively. In a catalytic cycle involving a dihydride species, however, carbonyl insertion may occur statistically in either of the two M−H bonds. Since hydroxide protons exchange rapidly with solvent protons, and since the transfer hydrogenation is a fully reversible process, the degree of deuterium incorporation in the product alcohol must be lower than 50% and, after prolonged reaction time, approach zero. Pàmies and Bäckvall illustrated this principle by monitoring the racemization of monodeuterated *S*-phenethyl alcohol with acetophenone in the presence of different late transition metal catalysts and found that the Ir and Rh catalysts under study uniformly followed a monohydride pathway.[19]

In our studies, we have moved from monodeuterated chiral donor substrates to cheaper and more readily available monodeuterated cyclohexanol (Cy-OH-d_1, eq 4). Reduction of cyclohexanone by $LiAlD_4$ followed by an aqueous workup provided Cy-OH-d_1 with deuterium incorporation at the desired position that exceeded 98% (^{1}H NMR and ^{13}C NMR).[20] In commercially available

(19) Pàmies, O.; Bäckvall, J.-E. *Chem. Eur. J.* **2001**, *7*, 5052.
(20) A similar approach combined with considerably more laborious analytical techniques (combustion instead of NMR) has been used to investigate the mechanism of the MPV reduction: Williams, E. D.; Krieger, K. A.; Day, A. R. *J. Am. Chem. Soc.* **1953**, *75*, 2404.



(4)

nondeuterated cyclohexanol, **2c**-catalyzed hydrogen transfer to acetophenone has been shown to be complete within 4 h (Table 3, entry 12). Under identical conditions but with cy-OH-d_1 as solvent, we see comparable rates of hydrogen transfer. NMR analysis of the product revealed the predominant formation of monodeuterated phenethyl alcohol where the degree of deuteration at carbinol position was ca. 90%. Extended reaction times did not influence the degree of deuteration in the product, indicating that no deuterium is transferred to the rapidly exchanging OH group. This accords with a monohydride mechanism as in related iridium(diphosphine) catalysts.[19]

The special case in the monohydride pathway involving concomitant hydride and proton transfer can be excluded in our system, since we do not have a pendant proton carrier group in our bis-carbene ligand.[21] Experimentally, this is evidenced by the high dependence of catalyst activity on the KOH concentration and by the fact that base-free runs did not give any hydrogenated product (see Table 3, entry 8). While we cannot rule out a direct, MPV-type hydride transfer, we prefer a metal-hydride as the active species because of the intramolecular transfer hydrogenation of allylbenzene we saw (cf. eq 3), which cannot occur via a direct hydride transfer.[22] Another indication against a MPV type mechanism is that the rate of reactivity of substituted acetophenones does not correlate with relative rates seen in MPV chemistry.[23] Finally, the forward reaction (i.e., substrate reduction) is considerably faster than the reverse reaction (substrate oxidation), while organic MPV reduction and Oppenauer oxidation are comparable in rates.[24]

By analogy with prior proposals, we conclude that the carboxylate ligand readily dissociates in the presence of the more strongly coordinating isopropoxide ligands (Scheme 2).[25] Apparently, the carbene ligands are sufficiently stable in the presence of the proposed intermediate hydrides so as not to reductively eliminate with loss of imidazolium salt.

Conclusions

We have developed new air-stable and moisture-insensitive Ir catalysts for efficient transfer hydrogenation. While for most other hydrogen transfer catalysts rhodium is more active than iridium, we find the opposite is true for these bis-carbenes. This may be a consequence of the carbene ligands having different electronic properties from the more frequently encountered phosphines. Ligand tuning in these chelating bis-carbene complexes is particularly convenient and provides an efficient methodology to increasing catalyst activity (R = neopentyl) or selectivity (R = isopropyl). The neopentyl group appears to be particularly useful in imparting satisfactory solubility characteristics and leads to remarkably higher activity than the other R groups. From reactivity studies and isotopic labeling, a monohydride hydrogen transfer mechanism is proposed.

Experimental Section

General Procedures. The *N*-alkylated imidazoles,[26] the ligand precursor **1a**,[27] and $[IrCl(cod)]_2$ [28] were prepared according to literature procedures; all other reagents are commercially available and were used as received. NMR spectra were recorded at 25 °C on Bruker spectrometers at 400 or 500 MHz (^{1}H NMR) and 100 or 125 MHz (^{13}C NMR), respectively, and referenced to $SiMe_4$ (δ in ppm, J in Hz). Assignments are based either on distortionless enhancement of polarization transfer (DEPT) experiments or on homo- and heteronuclear shift correlation spectroscopy. (Chiral) GC analysis was performed on a Hewlett-Packard 5890A gas chromatograph with a Cyclodex-B chiral column. Melting points are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA); residual solvent molecules have been identified by ^{1}H NMR.

Methylenebis(*N*-*n*-butyl)imidazolium Diiodide (1b). A solution of *N*-*n*-butylimidazole (2.50 g, 20 mmol) and CH_2I_2 (2.67 g, 10 mmol) was stirred in refluxing toluene (30 mL) for 24 h. The formed precipitate was collected by filtration and recrystallized from hot MeOH at −20 °C to give **1b** as an off-white solid (4.24 g, 82%). ^{1}H NMR (dmso-d_6, 500 MHz, $SiMe_4$): δ 9.44 (s, 2H, NCHN), 8.00 (s, 2H, H_{imid}), 7.91 (s, 2H, H_{imid}), 6.62 (s, 2H, CH_2), 4.23 (t, $^3J_{HH}$ = 7.2 Hz, 4H, $CH_2CH_2CH_2CH_3$), 1.79 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.29 (m, 4H, $CH_2CH_2CH_2CH_3$), 0.91 (t, $^3J_{HH}$ = 7.4 Hz, 6H, $CH_2CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR (dmso-d_6, 125 MHz, $SiMe_4$): δ 137.41 (NCN), 123.18 (C_{imid}), 122.16 (C_{imid}), 58.36 (NCH_2N), 49.04 ($CH_2CH_2CH_2CH_3$), 31.04 ($CH_2CH_2CH_2CH_3$), 18.72 ($CH_2CH_2CH_2CH_3$), 13.27 ($CH_2CH_2CH_2CH_3$). Mp: 153 °C. Anal. Calcd for $C_{15}H_{26}I_2N_4$ (516.20): C 34.90, H 5.08, N 10.85. Found: C 34.97, H 5.14, N 10.73.

Methylenebis(*N*-isopropyl)imidazolium Diiodide (1c). A solution of *N*-isopropylimidazole (2.45 g, 22 mmol) and CH_2I_2 (2.95 g, 11 mmol) was stirred in refluxing toluene (15 mL) for

(21) Noyori, R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931.

(22) Further support for the presence of metal-bound hydrides comes from in situ analysis of the catalytic hydrogenation of acetophenone in $(CD_3)_2CHOH$ at high catalyst loading (10 mol % **2c**). The ^{1}H NMR spectrum recorded after 10 min at 70 °C shows a resonance at −17.4 ppm, which disappears within 30 min. Unfortunately, any attempts to stabilize this hydrid species for detailed analysis were unsuccessful.

(23) However, Hammett correlation has been observed in MPV reduction, see: (a) Pickart, D. E.; Hancock, C. K. *J. Am. Chem. Soc.* **1955**, *77*, 4642. (b) Yager, B. J.; Hancock, C. K. *J. Org. Chem.* **1965**, *30*, 1174. (c) Csurös, Z.; Kálmán, V.; Lengyel-Mészáros, A.; Petró, J. *Period. Polytech., Chem. Eng.* **1968**, *12*, 161.

(24) Doering, W. von E.; Aschner, T. C. *J. Am. Chem. Soc.* **1953**, *75*, 393.

(25) Daley, C. J. A.; Bergens, S. H. *J. Am. Chem. Soc.* **2002**, *124*, in press.

(26) Gridnev, A. A.; Mihaltseva, I. M. *Synth. Commun.* **1994**, *24*, 1547.

(27) Claramut, R. M.; Elguero, J.; Meco, T. *J. Heterocycl. Chem.* **1983**, *20*, 1245.

(28) Lin, J.; Nomiya, K.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 6040.

(29) (a) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33. (b) Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421.

(30) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF program system*; Technical report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1992.

(31) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

(32) Spek, A. L. *PLATON*, A Multipurpose Crystallographic Tool; Utrecht University: The Netherlands, 2000.

20 h. The formed precipitate was collected by filtration and recrystallized twice from hot MeOH at −20 °C to give **1c** as a colorless solid (4.80 g, 89%). ^{1}H NMR (dmso-d_6, 400 MHz, $SiMe_4$): δ 9.51 (s, 2H, NCHN), 8.04 (s, 4H, H_{imid}), 6.60 (s, 2H, CH_2), 4.71 (septet, $^3J_{HH}$ = 6.6 Hz, 2H, $CHMe_2$), 1.50 (d, $^3J_{HH}$ = 6.6 Hz, 12H, $CHCH_3$). $^{13}C\{^1H\}$ NMR (dmso-d_6, 100 MHz, $SiMe_4$): δ 136.47 (NCN), 122.39 (C_{imid}), 121.36 (C_{imid}), 58.25 (CH_2), 52.82 ($CHMe_2$), 22.09 ($CHCH_3$). Mp: 228−230 °C (dec). Anal. Calcd for $C_{13}H_{22}I_2N_4$ (488.15): C 31.99, H 4.54, N 11.48. Found: C 31.98, H 4.53, N 11.41.

Methylenebis(*N*-neopentyl)imidazolium Diiodide (1d). A solution of *N*-neopentylimidazole (1.63 g, 11.8 mmol) and CH_2I_2 (1.49 g, 5.5 mmol) was stirred in refluxing toluene (15 mL) for 20 h. The formed precipitate was collected by filtration and recrystallized from hot MeOH at −20 °C to give **1d** as an off-white solid (2.37 g, 79%). ^{1}H NMR (dmso-d_6, 400 MHz, $SiMe_4$): δ 9.42 (s, 2H, NCHN), 8.00 (s, 2H, H_{imid}), 7.93 (s, 2H, H_{imid}), 6.60 (s, 2H, NCH_2N), 4.05 (s, 4H, CH_2CMe_3), 0.93 (s, 18H, CCH_3). $^{13}C\{^1H\}$ NMR (dmso-d_6, 125 MHz, $SiMe_4$): δ 137.93 (NCN), 124.74 (C_{imid}), 121.68 (C_{imid}), 59.83 (CH_2CMe_3), 58.45 (NCH_2N), 31.93 (CH_2CMe_3), 26.50 (CCH_3). Mp: 272−275 °C (dec). Anal. Calcd for $C_{17}H_{30}I_2N_4$ (544.26): C 37.52, H 5.56, N 10.29. Found: C 37.39, H 5.66, N 10.16.

Methylenebis(*N*-benzyl)imidazolium Diiodide (1e). A solution of *N*-benzylimidazole (2.35 g, 14.8 mmol) and CH_2I_2 (2.00 g, 7.4 mmol) was stirred in refluxing toluene (15 mL) for 20 h. The formed precipitate was collected by filtration and recrystallized from hot MeOH at −20 °C to give **1e** as an off-white solid (3.06 g, 70%). ^{1}H NMR (dmso-d_6, 400 MHz, $SiMe_4$): δ 9.51 (s, 2H, NCHN), 8.02 (s, 2H, H_{imid}), 7.90 (s, 2H, H_{imid}), 7.45−7.40 (m, 5H, H_{aryl}), 6.62 (s, 2H, NCH_2N), 5.50 (s, 2H, CH_2Ph). $^{13}C\{^1H\}$ NMR (dmso-d_6, 125 MHz, $SiMe_4$): δ 137.64 (NCN), 134.01 (C_{ipso}), 128.98 (C_{ortho}), 128.89 (C_{para}), 128.55 (C_{meta}), 123.24 (C_{imid}), 122.54 (C_{imid}), 58.49 (NCH_2N), 52.32 (CH_2Ph). Mp: 248−279 °C (dec). Anal. Calcd for $C_{21}H_{22}I_2N_4$ (584.24): C 43.17, H 3.80, N 9.59. Found: C 43.10, H 3.79, N 9.56.

Methylenebis(*N*-*tert*-butyl)imidazolium Diiodide (1f). A solution of *N*-*tert*-butylimidazole (4.18 g, 17 mmol) and CH_2I_2 (4.50 g, 17 mmol) was stirred in refluxing toluene (40 mL) for 20 h. The formed precipitate was collected by filtration and recrystallized twice from hot MeOH at −20 °C to give **1f** as a colorless solid (6.22 g, 72%). ^{1}H NMR (dmso-d_6, 400 MHz, $SiMe_4$): δ 9.58 (s, 2H, H_{imid}), 8.18 (s, 2H, H_{imid}), 8.10 (s, 2H, H_{imid}), 6.58 (s, 2H, CH_2), 1.62 (s, 18H, CCH_3). $^{13}C\{^1H\}$ NMR (dmso-d_6, 100 MHz, $SiMe_4$): δ 136.21 (NCN), 122.48 (C_{imid}), 121.08 (C_{imid}), 60.29 (CMe_3), 58.08 (CH_2), 28.71 (CCH_3). Mp: 238−239 °C (dec). Anal. Calcd for $C_{15}H_{26}I_2N_4$ (516.20): C 35.05, H 5.52, N 10.22. Found: C 34.72, H 5.31, N 10.30.

General Procedure for the Metalation. A mixture of ligand (1 mol equiv), $[IrCl(cod)]_2$ (0.5 mol equiv), KI (2 mol equiv), and NaOAc (4 mol equiv) was stirred in MeCN at reflux temperature for 16 h. After cooling, all volatiles were removed under reduced pressure and the residue was purified by column chromatography.

Methylenebis((*N*-methyl)imidazole-2-ylidene)acetato (Diiodo)Ir(III) (2a). 2a was formed according to the general procedure, starting from **1a** (104 mg, 0.24 mmol), $[IrCl(cod)]_2$ (79 mg, 0.12 mmol), KI (156 mg, 0.94 mmol), and NaOAc (115 mg, 1.4 mmol). Gradient column chromatography (SiO_2; first CH_2Cl_2 then CH_2Cl_2/acetone, 8:1) gave the title product as an orange solid (33 mg, 21%), which was crystallized from CH_2Cl_2/Et_2O. ^{1}H NMR (acetone-d_6, 400 MHz, $SiMe_4$): δ 7.36 (low-field part of AB d, $^3J_{HH}$ = 2.0 Hz, 2H, H_{imid}), 7.35 (high-field part of AB d, $^3J_{HH}$ = 2.0 Hz, 2H, H_{imid}), 6.37 (s, 2H, CH_2), 3.99 (s, 6H, NCH_3), 1.87 (s, 3H, CH_3COO). $^{13}C\{^1H\}$ NMR (acetone-d_6, 100 MHz, $SiMe_4$): δ 189.53 (CH_3COO), 127.48 (C−Ir), 124.34 (C_{imid}), 120.97 (C_{imid}), 62.85 (CH_2), 37.80 (NCH_3), 25.87 (CH_3COO). Anal. Calcd for $C_{11}H_{15}I_2N_4O_2Ir$ (681.29): C 19.39, H 2.22, N 8.22. Found: C 19.87, H 2.22, N 8.05.

Methylenebis((*N*-*n*-butyl)imidazole-2-ylidene)acetato (Diiodo)Ir(III) (2b). 2b was formed according to the general procedure, starting from **1b** (144 mg, 0.28 mmol), $[IrCl(cod)]_2$ (335 mg, 0.50 mmol), KI (183 mg, 1.1 mmol), and NaOAc (166 mg, 2.0 mmol). After stirring for 40 h at reflux, the volatiles were removed and the residue was suspended in CH_2Cl_2/pyridine (5:1 v/v, 20 mL). After filtration, Et_2O was carefully layered onto the filtrate, which caused slow crystallization of the title product as orange needles. Yield: 278 mg (73%). ^{1}H NMR ($CDCl_3$, 500 MHz, $SiMe_4$): δ 7.02 (d, $^3J_{HH}$ = 2.1 Hz, 2H, H_{imid}), 6.93 (d, $^3J_{HH}$ = 2.1 Hz, 2H, H_{imid}), 6.11 (s, 2H, NCH_2N), 4.42 (t, $^3J_{HH}$ = 7.6 Hz, 4H, $CH_2CH_2CH_2CH_3$), 2.02 (s, 3H, CH_3COO), 1.87 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.50 (m, 4H, $CH_2CH_2CH_2CH_3$), 0.99 (t, $^3J_{HH}$ = 7.4 Hz, 6H, $CH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, $SiMe_4$): 190.06 (CH_3COO), 127.45 (C−Ir), 121.72 (C_{imid}), 119.22 (C_{imid}), 62.42 (NCH_2N), 50.06 ($CH_2CH_2CH_2CH_3$), 33.06 ($CH_2CH_2CH_2CH_3$), 25.93 (CH_3COO), 19.91 ($CH_2CH_2CH_2CH_3$), 13.86 ($CH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{17}H_{27}I_2N_4O_2Ir$ (765.45): C 26.67, H 3.56, N 7.32. Found: C 26.91, H 3.50, N 7.23.

Methylenebis((*N*-isopropyl)imidazole-2-ylidene)acetato (Diiodo)Ir(III) (2c). 2c was formed according to the general procedure, starting from **1a** (407 mg, 0.83 mmol), $[IrCl(cod)]_2$ (270 mg, 0.40 mmol), KI (330 mg, 2.0 mmol), and NaOAc (328 mg, 4.0 mmol). Gradient column chromatography (SiO_2; first CH_2Cl_2 then CH_2Cl_2/acetone, 10:1) gave the title product as an orange solid (335 mg, 57%). Crystallization from CH_2Cl_2/Et_2O afforded analytically pure material. ^{1}H NMR ($CDCl_3$, 500 MHz, $SiMe_4$): δ 7.08 (d, $^3J_{HH}$ = 2.1 Hz, 2H, H_{imid}), 7.00 (d, $^3J_{HH}$ = 2.1 Hz, 2H, H_{imid}), 6.13 (s, 2H, CH_2), 5.48 (septet, $^3J_{HH}$ = 6.7 Hz, 2H, $CHMe_2$), 2.04 (s, 3H, CH_3COO), 1.50 (d, $^3J_{HH}$ = 6.7 Hz, $CHCH_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6, 125 MHz, $SiMe_4$): δ 190.19 (CH_3COO), 126.33 (C−Ir), 119.68 (C_{imid}), 117.96 (C_{imid}), 62.48 (CH_2), 51.00 ($CHMe_2$), 23.52 ($CHCH_3$), 22.62 (CH_3COO). Anal. Calcd for $C_{15}H_{23}I_2N_4O_2Ir$ (737.39): C 24.43, H 3.14, N 7.60. Found: C 24.44, H 3.24, N 7.44.

Methylenebis((*N*-neopentyl)imidazole-2-ylidene)acetato (Diiodo)Ir(III) (2d). 2d was formed according to the general procedure, starting from **1d** (245 mg, 0.60 mmol), $[IrCl(cod)]_2$ (198 mg, 0.30 mmol), KI (99 mg, 0.6 mmol), and NaOAc (100 mg, 1.2 mmol). Column chromatography (SiO_2; CH_2Cl_2) gave the title product as an orange solid (339 mg, 88%). Crystalline material was obtained by slow pentane diffusion into a CH_2Cl_2 solution of **2d**. ^{1}H NMR ($CDCl_3$, 500 MHz, $SiMe_4$): δ 7.07 (d, $^3J_{HH}$ = 2.2 Hz, 2H, H_{imid}), 6.95 (d, $^3J_{HH}$ = 2.1 Hz, 2H, H_{imid}), 6.14 (s, 2H, NCH_2N), 4.26 (s, 4H, CH_2CMe_3), 2.06 (s, 3H, CH_3COO), 1.09 (s, 18H, CCH_3). $^{13}C\{^1H\}$ NMR (acetone-d_6, 125 MHz, $SiMe_4$): δ 189.15 (CH_3COO), 127.61 (C−Ir), 123.45 (C_{imid}), 121.17 (C_{imid}), 62.83 (NCH_2N), 61.35 (CH_2CMe_3), 33.65 (CH_2CMe_3), 28.80 (CCH_3), 26.03 (CH_3COO). Anal. Calcd for $C_{19}H_{31}I_2N_4O_2Ir$ (793.50): C 28.76, H 3.94, N 7.06. Found: C 29.02, H 4.01, N 7.02.

Methylenebis((*N*-benzyl)imidazole-2-ylidene)acetato (Diiodo)Ir(III) (2e). 2e was formed according to the general procedure, starting from **1e** (592 mg, 1.0 mmol), $[IrCl(cod)]_2$ (335 mg, 0.50 mmol), KI (540 mg, 3.0 mmol), and NaOAc (365 mg, 4.5 mmol). After stirring for 40 h at reflux, the volatiles were removed and the residue was extracted with CH_2Cl_2 (3 × 5 mL). The combined organics were concentrated and purified by column chromatography (SiO_2; CH_2Cl_2/acetone, 6:1) to give **2e** as an orange solid (206 mg, 25%). Crystalline and analytically pure samples were obtained by liquid−liquid diffusion (CH_2Cl_2/pentane). ^{1}H NMR ($CDCl_3$, 400 MHz, $SiMe_4$): δ 7.53−7.50 (m, 4H, H_{meta}), 7.40−7.32 (m, 6H, $H_{ortho,para}$), 6.89 (d, $^3J_{HH}$ = 2.2 Hz, 2H, H_{imid}), 6.77 (d, $^3J_{HH}$ = 2.2 Hz, 2H, H_{imid}), 6.17 (s, 2H, NCH_2N), 5.67 (s, 4H, CH_2Ph), 2.00 (CH_3COO). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, $SiMe_4$): δ 190.45 (CH_3COO), 136.05 (C_{ipso}), 129.51 (C_{meta}), 128.86 (C_{ortho}), 128.29 (C_{para}), 128.16 (C−Ir), 121.68 (C_{imid}), 119.57 (C_{imid}), 62.52 (NCH_2N), 53.91 (CH_2Ph), 25.94 (CH_3COO). Anal. Calcd for

$C_{23}H_{23}I_2IrN_4O_2$ (833.48): C 33.14, H 2.78, N 6.72. Found: C 33.06, H 2.78, N 6.46.

Methylene((*N*-*tert*-butyl)imidazolium)((*N*-*tert*-butyl)-imidazole-2-ylidene)iodo(cyclooctadiene)iridium(I) Iodide (3f). 3f was formed according to the general procedure, starting from **1f** (520 mg, 1.00 mmol), $[IrCl(cod)]_2$ (335 mg, 0.50 mmol), KI (332 mg, 2.0 mmol), and NaOAc (330 mg, 4.0 mmol). Column chromatography (SiO_2; CH_2Cl_2/NEt_3, 100:3) gave the title product as a pale yellow solid (155 mg, 38%), which was crystallized from CH_2Cl_2/pentane. ^1H NMR ($CDCl_3$, 400 MHz, $SiMe_4$): δ 10.44 (t, $^3J_{HH} = 1.6$ Hz, 1H, NCHN), 8.68 (t, $^3J_{HH} = 1.8$ Hz, 1H, H_{imid-H}), 8.09 (d, $^3J_{HH} = 2.2$ Hz, 1H, $H_{imid-Ir}$), 7.80 (d, $^2J_{HH} = 12.9$ Hz, 1H, NCH_2N), 7.41 (d, $^2J_{HH} = 12.9$ Hz, 1H, NCH_2N), 7.25 (t, $^3J_{HH} = 1.8$ Hz, 1H, H_{imid-H}), 7.12 (d, $^3J_{HH} = 2.2$ Hz, 1H, $H_{imid-Ir}$), 4.86, 4.74, 2.98, 2.80 (4m, 4H, CH_{cod}), 2.2 (m, 4H, $CH_{2\ cod}$), 1.4 (m, 4H, $CH_{2\ cod}$), 1.84 (s, 9H, CCH_3), 1.74 (s, 9H, CCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, $SiMe_4$): δ 180.52 (C−Ir), 135.33 (NCHN), 124.04 (C_{imid-H}), 122.07 ($C_{imid-Ir}$), 120.97 ($C_{imid-Ir}$), 118.79 (C_{imid-H}), 82.58 (CH_{cod}), 81.06 (CH_{cod}), 61.96 (NCH_2N), 61.13 (CMe_3), 59.61 (CMe_3), 57.98 (CH_{cod}), 56.86 (CH_{cod}), 33.27 ($CH_{2\ cod}$), 32.30 (CCH_3), 31.97 ($CH_{2\ cod}$), 30.30 ($CH_{2\ cod}$), 30.12 ($CH_{2\ cod}$), 30.05 (CCH_3). Anal. Calcd for $C_{23}H_{37}I_2N_4Ir$ (815.59) × $0.25CH_2Cl_2$: C 33.37, H 4.52, N 6.70. Found: C 33.38, H 4.47, N 6.62.

Typical Procedure for Catalytic Transfer Hydrogenation. Ketone (2.0 mmol), catalyst (0.2 mL of a 10 mM solution in thf), KOH (0.1 mL of a mM solution in *i*PrOH), and *i*PrOH (10 mL) were placed in a 25 mL round-bottom flask in a preheated oil bath. Aliquots (0.2 mL) were taken at fixed times, quenched in hexane (4 mL), and filtered through a short path of SiO_2. The filtrate was subjected to GC analysis (volatile substrates/ketones) or evaporated to dryness and analyzed by ^1H NMR spectroscopy (nonvolatile ketones). Representative reactions were performed in the presence of diethylene glycol dibutyl ether (109 mg, 0.50 mmol) as ^1H NMR standard. For TOF_{50} measurements, the substrate solution was stirred 5 min at reflux temperature before catalyst and base were added. All data are averages of at least two runs.

Structure Determination and Refinement of 2c and 2d. Crystals were obtained after slow diffusion of pentane into a CH_2Cl_2 solution of the iridium(III) complexes. Data were collected on a Nonius KappaCCD (Mo Kα radiation) and corrected for absorption (SORTAV[29]). The structures were solved by Patterson methods (**2c**; DIRDIF92[30]) or by direct methods (**2d**; SIR92[31]) and refined on *F* for all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions. Relevant crystal and data parameters are presented in Table 7. Graphical illustrations and calculations were performed with the PLATON[32] package.

Table 7. Crystallographic Data for 2c and 2d

	2c	2d
color, shape	orange prism	orange needle
empirical formula	$C_{15}H_{23}I_2IrN_4O_2$	$C_{19}H_{31}I_2IrN_4O_2$
fw	737.40	793.51
radiation/Å	Mo Kα (monochr.) 0.71073	Mo Kα (monochr.) 0.71073
T/K	183	183
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/m$ (No. 11)
unit cell dimens		
a/Å	9.7205(7)	7.8889(4)
b/Å	15.2401(10)	14.9910(11)
b/Å	13.6460(10)	10.1801(6)
β/deg	94.946(4)	90.235(4)
V/Å^3	2014.0(2)	1203.91(11)
Z	4	2
D_{calc}/g cm^{-3}	2.432	1.520
μ/mm^{-1} (Mo Kα)	9.730	8.147
cryst size/mm	0.10 × 0.10 × 0.07	0.10 × 0.10 × 0.07
no. of total, unique reflns	10 472, 2029	7544, 1698
R_{int}	0.0642	0.0713
transmn range	0.447−0.515	0.409−0.557
no. of params, restraints	217, 0	136, 0
R,[a] R_w,[b] GOF	0.0355, 0.038, 0.785	0.034, 0.038, 0.941
resid density/e Å^{-3}	−1.03 < 0.99	−1.41 < 1.05

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, for all $I > 3\sigma(I)$. [b] $R_w = [\sum w(|F_o| - |F_c|)|^2/\sum F_o^2]^{1/2}$.

Acknowledgment. We thank Prof. Eduardo Peris (Castellon, Spain) for valuable information on the synthesis of the Rh analogues, the Swiss National Foundation (M.A.), and the U.S. DOE and NSF (J.W.F., R.H.C.) for financial support. We also thank Mr. Adrien Lavoie for GC assistance.

Supporting Information Available: Crystallographic details for **2c** and **2d**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020338X