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N-Heterocyclic Carbenes

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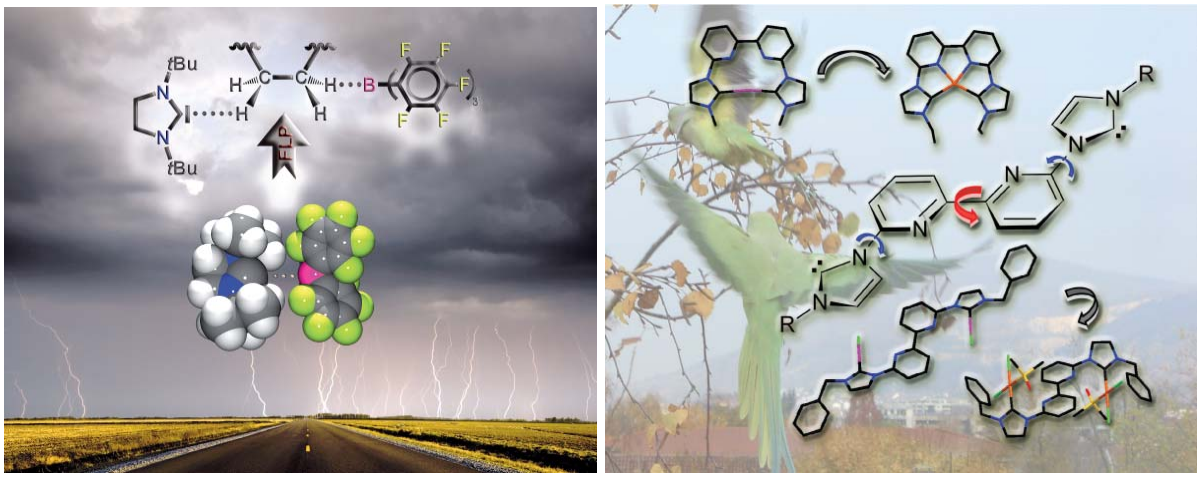

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N-heterocyclic carbenes of iridium(I): ligand effects on the catalytic activity in transfer hydrogenation†

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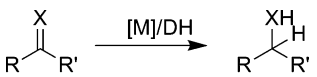
New Ir-NHC complexes based on different heterocyclic moieties like imidazole, benzimidazole and imidazolidine are presented and tested in transfer hydrogenation catalysis. A broad range of steric and electronic properties of NHC ligands is covered to give an idea for catalyst design from the experimental point of view.

Introduction

The reduction of organic compounds is an important research field in both academia and industry. It is gaining, however, additional importance due to the increasing use of renewable resources as feedstock for chemical industry. Many compounds available from such renewable resources are obtained in high oxidation states and need, at least in part, to be reduced. Several catalytic reactions useful for such processes *e.g.* hydrosilylation, classical hydrogenation, and transfer hydrogenation are well established (Scheme 1).[1] Transfer hydrogenation is a particularly useful and convenient catalytic process since there is no need for high dihydrogen pressure or hazardous reducing agents.[2]



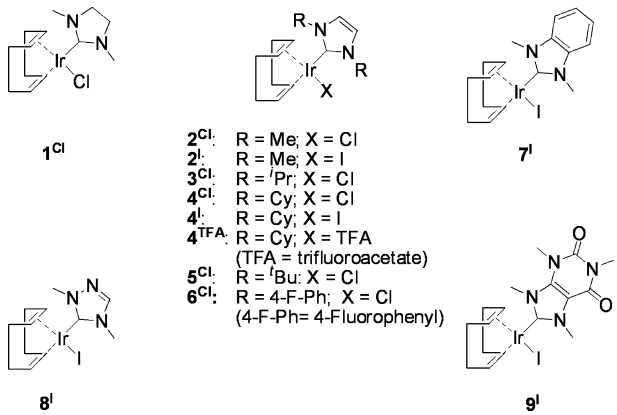
[M] = metal catalyst
DH = hydrogen donor

Scheme 1

Iridium and rhodium complexes have a long history as effective hydrogenation catalysts. Most prominent among them are Wilkinson's catalyst ($RhCl(PPh_3)_3$)[3] and Crabtree's catalyst ($[Ir(COD)(py)(PCy_3)]PF_6$, COD = 1,5-cyclooctadiene, py = pyridine).[4] Numerous other examples are also known in the literature.[5]

N-heterocyclic carbenes (NHC) are well established as efficient alternatives to phosphine ligands.[6] Their electronic properties, high thermal stability and strong coordination ability render them interesting as ligands for transition metal complexes. Accordingly, transfer hydrogenation has been successfully attempted and examined with NHC complexes of iridium.[7,8] However, several questions concerning the influence of steric and electronic properties of the NHC-ligands remain still open and deserve a detailed examination.

Many convenient synthetic routes to iridium complexes ligated either with NHCs,[9–13] or, more recently carbocyclic carbenes[8] above are known. In this work iridium catalysts are synthesized with a variety of NHC ligands and applied for transfer hydrogenation reactions (Scheme 2) in order to examine the influence of electronic, steric and other effects on the catalytic performance of their compounds.

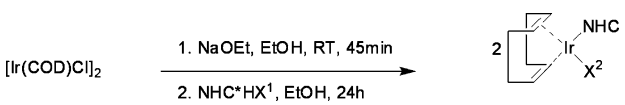


Scheme 2

Results and discussion

NHC complexes of iridium(I)

The new iridium complexes **1-Cl**, **4-I**, and **7-I** (Scheme 2) are synthesized by the so-called alkoxide route shown in Scheme 3.[11] The iridium precursor $[Ir(COD)OEt]_2$ is prepared *in situ* from



1-Cl, 4-I, 7-I

Scheme 3

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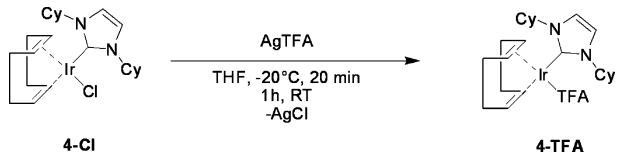
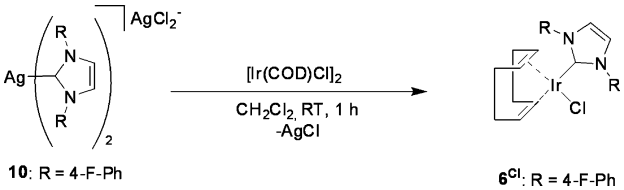
† Electronic supplementary information (ESI) available: Details of the X-ray crystallographic data and refinement of complexes **1-Cl** and **5-Cl**. CCDC reference numbers 726759 and 726760. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b906855d

$[Ir(COD)Cl]_2$ by reaction with sodium ethanolate in ethanol at ambient temperature. Further reaction with the azolium salt precursor (NHC·HX) results in the formation of the desired carbene complexes. It is noteworthy that preparation of **1-Cl** bearing the slightly stronger donating imidazolidin-2-ylidene ligands requires a particularly high excess of 1,3-dimethylimidazolidinium tetrafluoroborate (4 eq.). Preparation of **4-TFA** (TFA = trifluoroacetate) is conducted using **4-Cl** and AgTFA in a salt metathesis reaction; AgCl formed during the reaction, can be filtered off (Scheme 4). Preparation of **6-Cl** is carried out starting from $[Ir(COD)Cl]_2$ with the silver complex **10** as carbene source (Scheme 5).



4-Cl **4-TFA**

Scheme 4



10: R = 4-F-Ph **6^{Cl}**: R = 4-F-Ph

Scheme 5

The NHC complexes **1-Cl**, **4-I**, **4-TFA**, **6-Cl**, **7-I** and **10** were characterized by ^{1}H-NMR, ^{13}C-NMR and FAB/MS. Complexes **1-Cl** and the previously published compound **5-Cl**[14b] were additionally characterized by X-ray analysis (Fig. 1 and 2). The crystal structure of the latter compound has been published independently by another group in the meantime.[12i] The generation of the Ir-C bond is accompanied by the loss of a proton

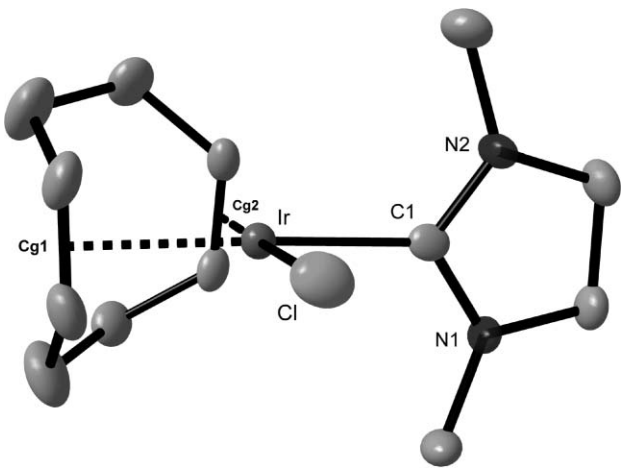


Fig. 1 Diamond plot[15] of compound **1-Cl** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ir–Cl 2.352(1), Ir–C1 2.018(4), Ir–Cg1 2.080, Ir–Cg2 1.982, C1–N1 1.335(5), C1–N2 1.342(6); Cl–Ir–C1 90.1(1), Cl–Ir–Cg1 91.5, Cl–Ir–Cg2 178.1, C1–Ir–Cg1 177.3, C1–Ir–Cg2 91.2, Cg1–Ir–Cg2 87.3, N1–C1–N2 107.8(4). Cg1 and Cg2 define the midpoints of the double bonds in the COD ligand.

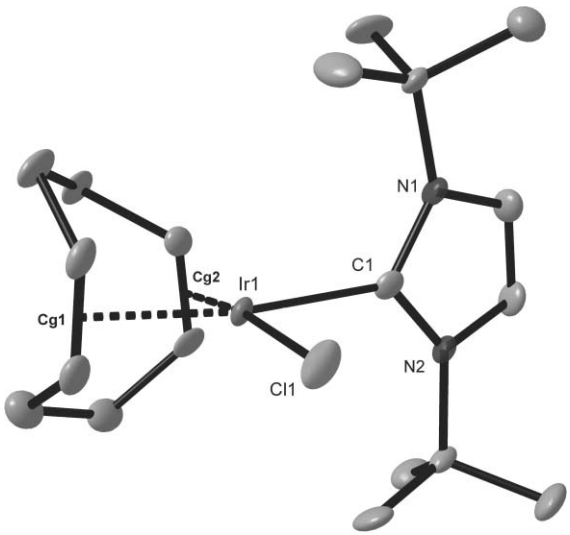
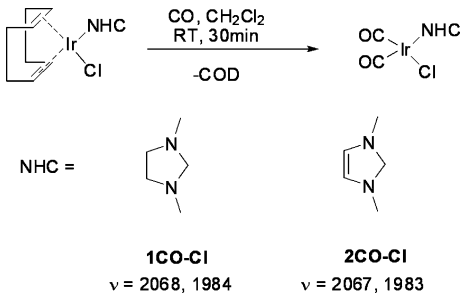


Fig. 2 Diamond plot[15] of molecule **A** of compound **5-Cl** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ir1–Cl1 2.382(2)/*2.385(2)*, Ir1–C1 2.069(6)/*2.063(6)*, Ir1–Cg1 2.036/*2.068*, Ir1–Cg2 1.984/*1.988*, C1–N1 1.376(8)/*1.362(8)*, C1–N2 1.375(7)/*1.393(9)*; Cl1–Ir1–C1 92.1(2)/*92.5(2)*, Cl1–Ir1–Cg1 89.8/*89.2*, Cl1–Ir1–Cg2 173.5/*174.7*, C1–Ir1–Cg1 172.4/*176.6*, C1–Ir1–Cg2 91.8/*91.7*, Cg1–Ir1–Cg2 87.2/*86.7*, N1–C1–N2 104.0(5)/*104.6(5)*. The corresponding values for the second crystallographic independent molecule **B** are given in *italics*. Cg1 and Cg2 define the midpoints of the double bonds in the COD ligand.

on C1 as observed in the ^{1}H-NMR spectra. The ^{13}C-NMR spectra show the carbene signals for the imidazol-2-ylidene ligands in the area between 176 and 182 ppm, as expected for Ir-C carbon atoms.[14b] In comparison to the imidazol-2-ylidene ligands, the carbene signals for the azolinylidene ligands in **1-Cl**, **7-I** (208.4 ppm, 192.7 ppm) appear significantly down field shifted. This, however, cannot be ascribed to the donor strengths of the ligands, as the CO signals in the IR-spectra of benzimidazol-2-ylidene, imidazol-2-ylidene, and imidazolidin-2-ylidene rhodium complexes ($Rh(NHC)I(CO)_2$) differ only marginally.[14] Moreover, the benzimidazol-2-ylidene has been assumed to be a weaker donor than the imidazol-2-ylidene. Spin multiplicity for the ^{13}C-NMR signals at 161.2 ($^2J_{CF}$ = 35.9 Hz) and 118.1($^1J_{CF}$ = 289 Hz) caused by C-F coupling prove the almost quantitative formation of **4-TFA** *via* salt metathesis.

The corresponding carbonyl substituted iridium complexes **1CO-Cl** and **2CO-Cl** are obtained by passing carbon monoxide through a dichloromethane solution of the COD substituted complexes **1-Cl** and **2-Cl** at room temperature. These complexes were produced in order to compare the donor strengths of saturated imidazolidin-2-ylidene and unsaturated imidazol-2-ylidene ligands (Scheme 6). The products are formed almost quantitatively within 30 min due to the strong donor capability of the NHC ligands.[14]

The *cis*-conformation of both of the carbonyl ligands in complexes **1CO-Cl** and **2CO-Cl** was confirmed by both IR and NMR spectroscopy. The IR spectra exhibit two strong ν(CO)-bands. Each ^{13}C-NMR-spectrum shows two signals between δ = 168 and 183 ppm attributed to the CO carbon atom. As observed for the COD complexes **1-Cl** and **2-Cl**, the carbene signals of

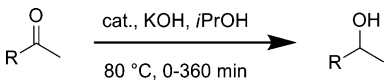


Scheme 6

1CO-Cl (199.3 ppm) and **2CO-Cl** (174.7 ppm) differ significantly. However, IR data confirm the donor strength of the imidazol-2-ylidene and the imidazolidin-2-ylidene ligands being quite similar.

Catalytic transfer hydrogenation

Complexes **1-Cl**–**9-I** were examined in transfer hydrogenations of selected ketones with *i*PrOH as hydrogen donor to get deeper insights in how to design highly efficient catalysts of formula Ir(COD)(X)(NHC) for this catalytic reaction (Scheme 7). The reaction conditions are described in detail in the experimental part.



Scheme 7

The product yields of all examined catalysts applying acetophenone (R = Ph in Scheme 7), as the substrate are summarized in Table 1.

It has to be noted that different catalysts display a different activation period before the actual reaction starts. This has to be accounted for when determining the activity of the catalysts, expressed by the turnover frequency (TOF, given in time^{-1}). Giving a turnover number (TON, no unit) is misleading in this context because it expresses the maximum number of catalytic cycles a catalyst can perform before its decomposition.[16] TOFs and TONs have been mixed up in the literature quite frequently.

Table 1 Transfer hydrogenation with complexes **1-Cl**–**9-I**[a]

Entry	Catalyst	Yield [%] after 10 min	Yield [%] after 120 min
1	**4-Cl**	94	96
2	**4-I**	5	96
3	**4-TFA**	80	96
4	**8-I**	4	92
5	**7-I**	3	93
6	**3-Cl**	91	96
7	**6-Cl**	31	87
8	**2-Cl**	63	97
9	**2-I**	4	73
10	**9-I**	19	84
11	**1-Cl**	37	98
12	**5-Cl**	3	68
13	—	0	0(1)[b]

[a] Reaction conditions: S/C/B = 1000/10/100 with 0.6 mmol of acetophenone and 0.06 mmol of KOH in 5 mL of *i*PrOH at 80 °C; yields determined by GC. [b] Yield after 360 min.

We did not determine TONs in this work, since the catalyst was usually not recovered after one catalytic run, but did not decompose during this time.

Due to different activation periods not all of the catalysts show high yields after 10 min, however, almost all of them reach good product yields (68–98%) within 2 h. No deactivation of the catalyst occurs. Without catalyst no significant product formation is determined even after 6 h (Entry 13).

In order to get a deeper insight in the catalytic transfer hydrogenation reaction with complexes of the general formula Ir(COD)(X)(NHC) several reaction and catalyst parameters were varied. These variations include catalyst concentrations, the applied ligands X, the NHC donor strength, the NHC steric bulk and the substrate influence.

Catalyst concentration

Judging from Table 1, complex **4-Cl** appears to be a very active catalyst without a pronounced initiation period. Therefore, the catalyst concentration was reduced by the factor 100 (to 1000:100:0.01 substrate:base:catalyst). Under the latter conditions a considerable initiation period (20 min) is detectable, showing that the comparatively high catalyst concentration in the 100:10:1 (substrate:base:catalyst) case ensures enough catalyst molecules to be present to start the reaction with an initiation period of only *ca.* 5 min (see Fig. 3). With significantly less catalyst molecules present transport phenomena obviously dominate the initial period until the catalytic reaction reaches its full potential. After this initiation period the catalytical activities for both catalyst concentrations are indistinguishable within the measurement errors (TOFs ~ 1000 h^{-1}).

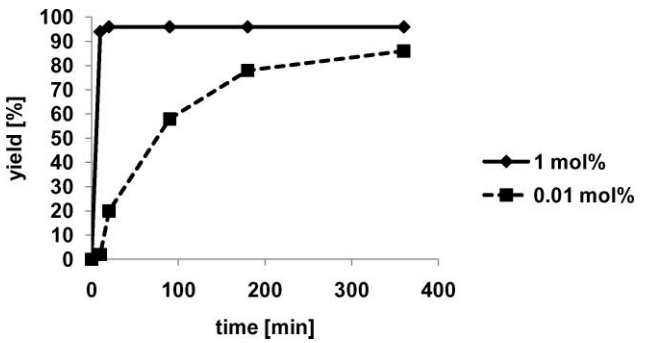


Fig. 3 Varying catalyst concentrations (reaction conditions: S/C/B = 1000/10/100 (1 mol% **4-Cl**) or S/C/B = 1000/0.1/100 (0.01 mol% **4-Cl**) with 0.6 mmol of acetophenone and 0.06 mmol of KOH in 5 mL of *i*PrOH at 80 °C; yields determined by GC).

In the case of lower catalyst concentration, however, after a reaction time of *ca.* 20 min the reaction velocity slows down increasingly, most likely due to transport phenomena in the substrate depleted surrounding of the catalyst molecules. Accordingly, it takes much more time (180 min instead of 10 min) to reach good yields (>80%) with lower concentration.

Influence of the ligand X

Again to be compared with complex **4-Cl** the derivatives **4-I** and **4-TFA** were examined in more detail with respect to their reaction kinetics (Fig. 4). The most obvious difference is again the length

initiation period. While **4-Cl** and **4-TFA** display a short initiation period to reach full activity. Compound **4-I** takes much longer to get activated. It is very interesting to note the high activity of all three compounds (**4-TFA** *ca.* 960 h^{-1}, **4-Cl** *ca.* 1260 h^{-1} and **4-I** *ca.* 2200 h^{-1}). Furthermore, in all three cases conversions of >90% are reached within 15 min, or within 10 min after the "takeoff" of the catalytic reaction. The still existing differences in activity might be due to the close proximity of the former ligand as a counter ion, exercising still some influence on the (catalytic) reaction.

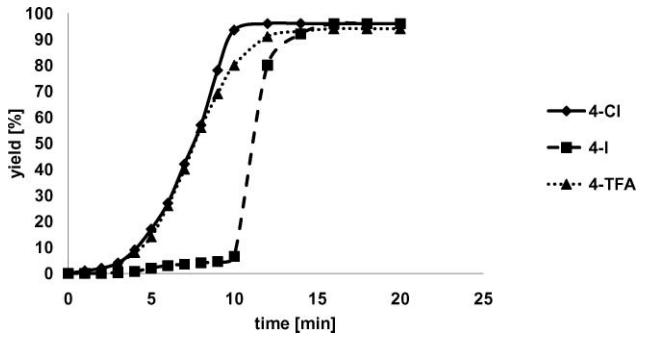


Fig. 4 Anion influence of the catalysts (reaction conditions: S/C/B = 1000/10/100 with 0.6 mmol of acetophenone and 0.06 mmol of KOH in 5 mL of *i*PrOH at 80 °C; yields determined by GC).

Donor strength

When comparing the complexes **2-I**, **7-I**, **8-I** and **9-I**, with the donor strength of the NHC-ligand increasing in the order **9-I**<**8-I**<**7-I**<**2-I**[14a] it can be noted that compound **9-I** displays the shortest initiation period and the highest initial activity. Compound **8-I** has a somewhat longer initiation period than **9-I** but also a high initial activity. Complexes **7-I** and **2-I**, however, both display a longer initiation period and a lower activity, despite reaching similar product yields to **8-I** and **9-I** after prolonged reaction time. A weaker donor capability of the NHC-ligand seems to enhance the complex activity by both shortening the initiation time and, additionally, accelerating the catalytic reaction when acetophenone is the substrate. The results are shown in Fig. 5.

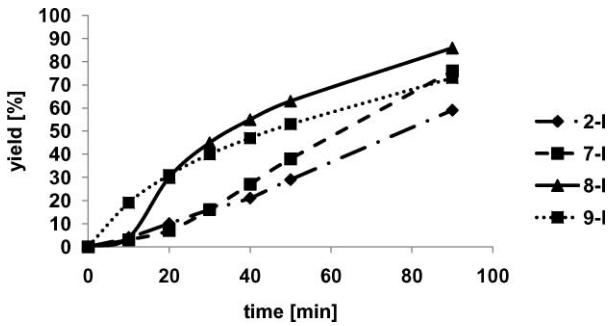


Fig. 5 Influence of donor strength in transfer hydrogenation (reaction conditions: S/C/B = 1000/10/100 with 0.6 mmol of acetophenone and 0.06 mmol of KOH in 5 mL of *i*PrOH at 80 °C; yields determined by GC).

The picture changes, however, when acetonaphtone is applied as substrate (Fig. 6). This influence of the carbene ligand with acetonaphtone is more pronounced than the effect observed with acetophenone. A possible explanation might be, at least on first

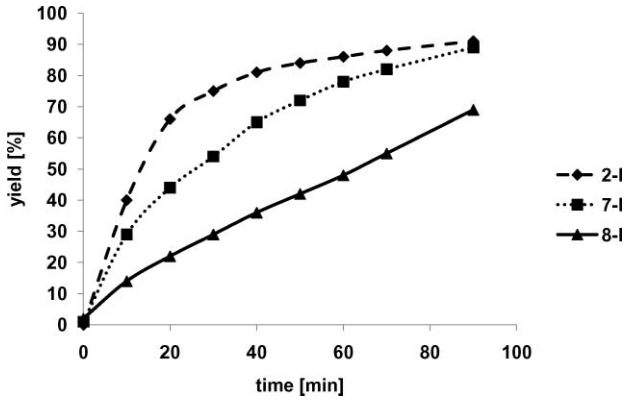


Fig. 6 Influence of donor strength in transfer hydrogenation (reaction conditions: S/C/B = 1000/10/100 with 0.6 mmol of acetonaphtone and 0.06 mmol of KOH in 5 mL of *i*PrOH at 80 °C; yields determined by GC).

glance, the difference in steric bulk between acetophenone and acetonaphtone. However, it appears that the catalyst (precursor) complex with the weaker donating carbene (**8-I**) shows in this case worse performance than the catalysts ligated with more strongly donating carbenes. The influence of the substrate obviously overcompensates the influence of the carbene ligand on the metal. Acetonaphtone with its larger aromatic moieties might be able to better stabilize the transition state, thus influencing the reaction velocity.

In 1982 Graziani *et al*. published a screening of different phosphine catalysts in transfer hydrogenation.[17] No relationship between donor strengths of the phosphines and catalyst activity could be observed in that case. Nolan *et al*. could not clearly distinguish between steric and electronic ligand effects.[18] It appears, however that such a distinction is possible.

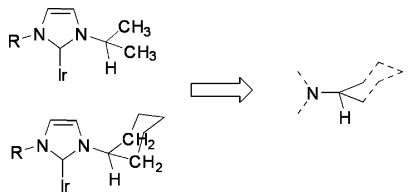
Steric properties

In order to examine the steric influence of the carbene ligands, four complexes **2-Cl** (with CH_3-groups on the NHC nitrogen-atoms), **3-Cl** (with *i*Pr-groups), **4-Cl** (with Cy-groups) and **5-Cl** with *t*Bu-groups were compared. The highest activity is obtained with **3-Cl** and **4-Cl**, having identical TOFs (>1000 h^{-1}) within the measurement errors. Compound **2-Cl** with the least bulky *N*-attached substituent displays at somewhat more pronounced activation time and after reaching a maximum TOF of only *ca.* 50 h^{-1} slows down even more.

The most bulky derivative **5-Cl** also shows the most pronounced activation period, reaches a maximum TOF of somewhat less than 100 h^{-1}, trailing off rather quickly. These observations might be explained by the pronounced similarity of the sterics of compounds **3-Cl** and **4-Cl** (see Scheme 8). The carbene ligand of compound **5-Cl** is seemingly bulky enough to slow down the approach of substrates, while compound **2-Cl** with the sterically least demanding ligands on the NHC-*N*-atoms might be unable to stabilize either the active species and/or the transition states (Fig. 7).

Variation of the substrates

Since the catalyst **4-Cl** displays the highest activity for the transfer hydrogenation of acetophenone, we tested **4-Cl** with



Scheme 8

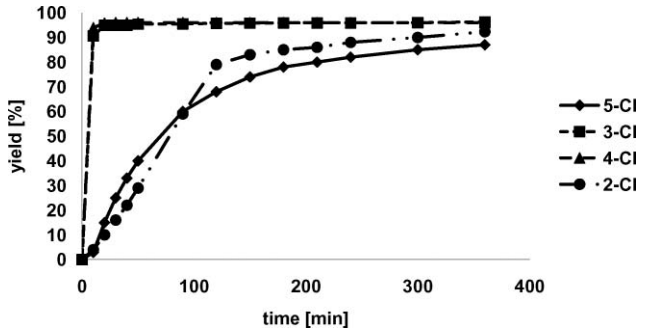


Fig. 7 Steric effects of the NHC ligands in transfer hydrogenation. In this particular case catalysts **3-Cl** and **4-Cl** are obviously identical with respect to the form of the kinetic curve (reaction conditions: S/C/B = 1000/10/100 with 0.6 mmol of acetophenone and 0.06 mmol of KOH in 5 mL of *i*PrOH at 80 °C; yields determined by GC).

several functionalized acetophenones (Table 2) which are more difficult to hydrogenate. The substrates were selected so as to have either electron donating or electron withdrawing moieties on the phenyl ring. According to the literature, no decomposition or side reactions of these substituted ketones in transfer hydrogenation has been detected.[19]

The reduction of 4-nitroacetophenone to its alcohol turns out to be particularly slow with **4-Cl** (Entry 1). Even after 6 hours only a moderate yield of 46% of the corresponding alcohol could be isolated. The yields for the other substituted acetophenones reach nearly full conversions after 20 minutes (Entries 2–6). The slightly lower yields compared to the standard reaction (94% of 1-phenylethanol after 10 minutes) can be explained by the electronic properties of the substrates. In contrast to previously published Ir-bis-carbene complexes,[20] a relationship between the electron withdrawing and the electron donating substituents on the phenyl ring can be seen. The more electron rich the substrates are, like methoxy or methyl, the faster the reaction with catalyst **4-Cl** is.

Table 2 Transfer hydrogenation with varying substrates[a]

Entry	Catalyst	Substrate	Yield [%] after 10 min	Yield [%] after 20 min
1	**4-Cl**	4-nitroacetophenone	8	46[b]
2	**4-Cl**	4-methoxy acetophenone	86	87
3	**4-Cl**	4-chloro acetophenone	48	97
4	**4-Cl**	4-trifluoromethyl acetophenone	5	99
5	**4-Cl**	4-methylacetophenone	87	96
6	**4-Cl**	acetonaphtone	93	95

[a] Reaction conditions: S/C/B = 1000/10/100 with 0.6 mmol of substrate in 5 mL of *i*PrOH at 80 °C; yields determined by GC. [b] Yield after 360 min.

Conclusion

A series of complexes of the general formula Ir(COD)X(NHC) was synthesized and examined in transfer hydrogenation. Steric and electronic effects of both ligands and substrate influence the catalytic reaction considerable. The reactions display an initiation period which seems to be dominated by the replacement of X by isopropanolate, indicating a concerted mechanism. The size of the *N*-attached ligands of the carbene moiety seems to be optimal when a small unit (H) and larger units (CH_3 or cyclohexyl) can rotate and adopt different positions during the course of the reaction, thereby possibly stabilizing the M-H intermediate with its small hydrogen ligand.

Theoretical calculations and the collection of additional kinetic data to fully establish the proposed mechanistic steps are currently under way in our laboratories. A better understanding of the different influences on the catalytic cycle will help to synthesize more active catalysts and pave the way to highly active chiral derivatives for chiral transfer hydrogenations with closely related iridium catalysts.

Experimental

All experiments were carried out under dry argon using standard Schlenk or glove box techniques. Solvents were dried by standard methods and distilled under nitrogen. ^{1}H, and ^{13}C NMR spectra were recorded on a JEOL-JMX-GX 400 MHz spectrometer at room temperature and referenced to the residual ^{1}H and ^{13}C signals of the solvents. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept. = septet, m = multiplet, br = broad signal. Coupling constants *J* are given in Hz. IR spectra were recorded on a Jasco 460 spectrometer. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. Mass spectra were performed at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 spectrometer using FAB technique. GC spectra were measured on a Varian gas chromatograph CP-3800 (column: FactorFour VF-5 ms) equipped with a FID detector. 1,3-Dimethylbenzimidazolium iodide,[21] 1,3-dicyclohexylimidazolium iodide[22] and 1,3-dimethylimidazolidinium tetrafluoroborate[23] were prepared according to reported procedures. The metal dimer precursor $[Ir(COD)Cl]_2$ was purchased from Strem. NHC complexes **2-I**,[10d] **2-Cl**,[12a] **3-Cl**, **4-Cl**, **5-Cl**, **8-I** and **9-I**[14] were prepared according to literature procedures.

1,3-Di-(4-fluorophenyl)imidazolium chloride

Paraformaldehyde (100 mmol) was suspended in 100 mL of toluene, and 4-fluoroaniline (100 mmol) was added dropwise. The slurry was cooled to 0 °C and 100 mmoL of 4-fluoroaniline and 100 mmol of HCl (3 N) were added. At room temperature, 100 mmol of glyoxal (40% aqueous solution) was added, and the reaction mixture was stirred for 12 h at 40 °C. The product was filtered, washed with THF and ether, and dried under vacuum. Yield: 40%. ^{1}H-NMR (270.2 MHz, 25 °C, DMSO-d_6): δ 10.49 (s, 1H, NCHN), 8.57 (s, 2 H, NC*H*C*H*N) 8.04 (m, 4H, H-Ar), 7.57 (m, 4H, H-Ar); ^{13}C{^{1}H}-NMR (100.5 MHz, 25 °C, DMSO-d_6): δ 162.96 (d, $^1J_{CF}$ = 245.7 Hz, *p*-FC), 135.6 (NCHN), 131.7 (d, $^4J_{CF}$ = 2.3 Hz, NC-Ar), 125.3 (d,$^3J_{CF}$ = 9.2 Hz, *o*-C), 122.7

(N*C*H*C*HN), 117.6 (d, $^2J_{CF}$ = 23.7 Hz, *m*-C); MS (FAB): [*m*/*z*]: 257 $[M]^+$.

Bis[1,3-di(4-fluorphenyl)imidazolin-2-yliden]silver(I) dichloroargenate (10)

1,3-Di-(4-fluorophenyl)imidazolium chloride (0.81 mmol) was dissolved in dichloromethane and silver(I) oxide (0.5 mmol) was added. The reaction mixture was heated at reflux for 4 h and the resulting suspension was filtered over a plug of Celite. The white product was precipitated with n-pentane and dried under vacuum. Yield: 61%. ^{1}H-NMR (270.2 MHz, 25 °C, DMSO-d_6): δ 8.07 (s, 2 H, NC*H*C*H*N), 7.80 (m, 4H, H-Ar), 7.39 (m, 4H, H-Ar); ^{13}C{^{1}H}-NMR (100.5 MHz, 25 °C, DMSO-d_6): δ 207.6 (NCHN), 162.4 (d, $^1J_{CF}$ = 244.7 Hz, *p*-FC), 136.58 (NC-Ar), 125.27 (d, $^3J_{CF}$ = 8.4 Hz, *o*-C), 122.70 (N*C*H$_2$*C*H$_2$N), 117.61 (d, $^2J_{CF}$ = 22.9 Hz, *m*-C); MS (FAB): *m*/*z* = 618.3 $[M - AgCl_2]^+$, 362.6 $[M - NHC - AgCl_2]^+$.

Chloro(η^4-1,5-cyclooctadiene)(1,3-dimethylimidazolidin-2-ylidene)iridium(I) (1-Cl)

NaH (0.6 mmol) was dissolved in 3 mL of ethanol and slowly added to a suspension of 0.15 mmol of $[Ir(COD)Cl]_2$ in 2 mL of ethanol. The reaction mixture was stirred for 45 min at room temperature and 1.2 mmol of 1,3-dimethylimidazolidinium tetrafluoroborate were added. After stirring for 24 h at room temperature, the solvent was removed *in vacuo*. The product was purified by column chromatography (silica, 1:2 AcOEt/*n*-pentane). Yield: 56%. ^{1}H-NMR (400 MHz, 25 °C, $CDCl_3$): δ 4.50 (br s, 2H, CH-COD), 2.96 (br s, 2H, CH-COD), 3.39 (s, 6H, NCH_3), 3.54 (d, 4H, N*C*H$_2$), 2.17 (m, 4H, CH_2-COD), 1.71(m, 2H, CH_2-COD), 1.57 (m, 2H, CH_2-COD). ^{13}C{^{1}H}-NMR (100.5 MHz, 25 °C, $CDCl_3$): δ 208.4 (Carbene-C), 85.4 (CH-COD), 51.5, 51.4 (NCH_2), 37.6 (NCH_3), 34.8, 30.0 (CH_2-COD). MS (FAB): *m*/*z* = 434.1 $[M]^+$; elemental analysis calcd. for $C_{13}H_{22}ClN_2Ir$: C 35.98, H 5.09, N 6.31; found: C 35.97, H 5.09, N 6.31.

Iodo(η^4-1,5-cyclooctadiene)(1,3-dicyclohexylimidazolin-2-yliden)iridium(I) (4-I)

NaH (0.6 mmol) was dissolved in 3 mL of ethanol and slowly added to a suspension of 0.15 mmol of $[Ir(COD)Cl]_2$ in 2 mL of ethanol. The reaction mixture was stirred for 45 min at room temperature and 3.2 mmol of 1,3-cyclohexylimidazolium iodide and 1.2 mmol of NaI were added. After stirring for 24 h at room temperature, the solvent was removed *in vacuo*. The product was purified by column chromatography (silica, 1:2 AcOEt/*n*-pentane). Yield: 81%. ^{1}H-NMR (400 MHz, 25 °C, $CDCl_3$): δ 6.84 (d, 2H, NC*H*C*H*N), 5.21 (tt, $^3J_{HH}$ = 14 Hz, 2H NCH-Cy), 4.73(m, 2H, CH-COD), 3.00 (m, 2H, CH-COD), 2.34 (m, 2H, CH_2-COD), 1.82 (d, $^3J_{HH}$ = 11.6, 2H, CH_2-COD), 2.16–1.16 (m, 4H, CH_2-COD, 20H,CH_2-Cy); ^{13}C{^{1}H}-NMR (100.5 MHz, 25 °C, $CDCl_3$): δ 176.7 (Carbene-C), 117.1 (N*C*H*C*HN), 81.5, 59.3 (CH-COD), 53.4 (CH-Cy), 34.6, 33.5, 33.2, 30.4, 26.1, 25.6, 25.4 (CH_2-Cy, CH_2-COD), MS (FAB): *m*/*z* = 659.9 $[M]^+$, 233 $[NHC]^+$; elemental analysis calcd. for $C_{23}H_{36}IIrN_2$: C 41.88, H 5.50, N 4.25; found: C 42.18, H 5.78, N 4.18.

Trifluoracetato(η^4-1,5-cyclooctadiene)(1,3-dicyclohexylimidazol-2-ylidene)iridium(I) (4-TFA)

4-Cl (0.1 mmol) was dissolved in THF and a solution of 0.1 mmol of silver trifluoroacetate in 4 mL of THF was added in small portions at –40 °C, while a voluminous precipitate of silver chloride formed. The reaction mixture was allowed to warm up to room temperature and stirred for 1 h. The yellow suspension was filtered and volatiles were removed *in vacuo*. The yellow product was extracted three times with 8 mL of hexane. The volatiles were again removed under vacuum. Yield: 91%. ^{1}H-NMR (400 MHz, C_6D_6, 25 °C): δ 6.29 (d, 2H, NC*H*CHN), 5.33 (tt, ^3J = 14 Hz, 2H, NCH-Cy), 4.76 (m, 2H, CH-COD), 3.03 (m, 2H, CH-COD), 2.34 (d, $^3J_{HH}$ = 12, 2H, CH_2-COD), 2.17 (m, 4H, CH_2-COD), 1.82 (d, $^3J_{HH}$ = 11.6, 2H, CH_2-COD), 1.71–1.04 (m, 20H, CH_2-Cy); ^{13}C{^{1}H}-NMR (100.5 MHz, 25 °C, C_6D_6): δ 176.74 (Carbene-C), 161.2 (q, $^1J_{CF}$ = 35.9, CO) 118.1(q, $^1J_{CF}$ = 289.9, CF_3), 117.1 (N*C*H*C*HN), 83.7, 60.5 (CH-COD), 49.5 (CH-Cy), 35.1, 34.1, 29.4, 26.3, 25.9, 25.6 (CH_2-Cy, CH_2-COD); MS (FAB): *m*/*z* = 645.9 $[M]^+$.

Chloro(η^4-1,5-cyclooctadiene)(1,3-di-(4-fluorphenyl)imidazolin-2-yliden)iridium(I) (6-Cl)

To a solution of the silver carbene complex **10** (0.10 mmol) in 20 mL of CH_2Cl_2, $[IrCl(COD)]_2$ (0.1 mmol) was added. The mixture was stirred for 6 h at room temperature. The yellow suspension was concentrated *in vacuo*. The product was purified by column chromatography (silica, 1:2 AcOEt/*n*-pentane). Yield: 70%. ^{1}H-NMR (270.2 MHz, 25 °C, C_6D_6): δ 7.87 (m, 4H, H-Ar), 7.74 (m, 4H, H-Ar), 6.29 (m, 2H, NC*H*C*H*N), 4.99 (m, 2H, CH-COD), 2.35 (m, CH-COD), 1.81 (m, 2H, CH_2-COD), 1.65 - 1.18 (m, 6H, CH_2-COD); ^{13}C{^{1}H}-NMR (100.5 MHz, 25 °C, C_6D_6): δ 182.6 (NCHN), 162.4 (d, $^1J_{CF}$ = 246.2 Hz, *p*-FC), 136.6 (NC-Ar), 121.5 (N*C*H*C*HN), 115.7 (d, $^2J_{CF}$ = 23 Hz, *m*-C), 84.7, 51.5 (CH-COD), 33.5, 29.7 (CH_2-COD); ^{13}C{^{1}H}-NMR (100.5 MHz, 25 °C, $CDCl_3$): δ 181.8 (NCHN), 162.2 (d, $^1J_{CF}$ = 246.7 Hz, *p*-FC), 136.1 (NC-Ar), 127.5 (d, $^3J_{CF}$ = 8.3 Hz, *o*-C), 122.1 (N*C*H*C*HN), 115.5 (d,$^2J_{CF}$ = 22.2 Hz, *m*-C), 84.4, 52.0 (CH-COD), 33.0, 29.2 (CH_2-COD); MS (FAB): *m*/*z* = 592.4 $[M]^+$; elemental analysis calcd. for $C_{23}H_{22}F_2ClIrN_2$: C 46.66, H 3.75, N 4.73; found: C 46.66, H 3.77, N 4.50.

Iodo(η^4-1,5-cyclooctadiene)(1,3-dimethylbenzimidazolin-2-ylidene)iridium(I) (7-I)

NaH (0.6 mmol) was dissolved in 3 mL of ethanol and slowly added to a suspension of 0.15 mmol of $[Ir(COD)Cl]_2$ in 2 mL of ethanol. The reaction mixture was stirred for 45 min at room temperature and 3.2 mmol of 1,3-dimethylbenzimidazolium iodide and 1.2 mmol of NaI were added. After stirring for 24 h at room temperature, the solvent was removed *in vacuo*. The product was purified by column chromatography (silica, 1:2 AcOEt/*n*-pentane). Yield: 81%. ^{1}H-NMR (400 MHz, 25 °C, $CDCl_3$,): δ 7.24 (m, 4H, CH-Ar), 4.88 (m, 2H, CH-COD), 2.99 (m, 2H, CH-COD), 4.07 (s, 6H, NCH_3), 2.19 (m, 4H, CH_2-COD), 1.86 (m, 2H, CH_2-COD), 2.00 (m, 2H, CH_2-COD), 1.43 (m, 2H, CH_2-COD); ^{13}C{^{1}H}-NMR (100.5 MHz, 25 °C, $CDCl_3$): δ 192.7 (Carbene-C), 135.4, 122,74, 109.7 (Ar-C), 134.9, 122.7, 110.31 (Ar-C), 85.2,

55.6 (CH-COD), 35.0, 33.0, 30.7 (NCH_3, CH_2-COD); MS (FAB): m/z = 573.8 $[M]^+$, 447.0 $[M - I]^+$, 147.1 $[NHC]^+$.

General procedure for carbonyl derivatives

CO gas (1 bar, 15 mL/min) was passed through a solution of the COD complex (0.17 mmol) in 15 mL of dichloromethane at room temperature for 15 min. The colour lightened. The solution was reduced to 5 mL *in vacuo* and *n*-hexane was added to precipitate the carbonyl complexes in high yields.

Dicarbonylchloro(1,3-dimethylimidazolidin-2-ylidene)iridium(I) (1CO-Cl)

Yield: 91%. IR (CH_2Cl_2): ν = 2068, 1984 cm^{-1}; ^{1}H-NMR (400 MHz, 25 °C, $CDCl_3$): δ 3.67 (s, 4H, NCH_2CH_2N), 3.30 (m, 6H, NCH_3); $^{13}C\{^1H\}$-NMR (100.5 MHz, 25 °C, $CDCl_3$): δ 199.3 (Carbene-C), 181.7, 168.1 (CO), 51.9 (NCH_2CH_2N), 37.4 (NCH_3); MS (FAB): m/z = 354.7 $[M - CO]^+$.

Dicarbonylchloro(1,3-dimethylimidazolin-2-ylidene)iridium(I) (2CO-Cl)

Yield: 89%. IR (CH_2Cl_2): ν = 2067, 1983 cm^{-1}; ^{1}H-NMR (400 MHz, 25 °C, Benzol-d_6): δ 5.59 (s, 2H, NC*H*C*H*N), 3.10 (s, 6H, NCH_3); $^{13}C\{^1H\}$-NMR (100.5 MHz, 25 °C, Benzol-d_6): δ 182.7 (CO), 174.7 (Carbene-C), 169.5 (CO), 121.74 (N*C*H*C*HN), 37.57 (NCH_3); MS (FAB): m/z = 352.7 $[M - CO]^+$.

Catalytic reactions

A ketone (0.6 mmol), 0.06 mmol of potassium hydroxide and 4 mL of *i*PrOH are placed in a Schlenk tube. Diethylene glycol dibutyl ether (375 μL) was added as an internal GC standard. The mixture was heated at 80 °C for 5 minutes and a catalyst solution (0.006 mmol or 0.00006 mmol of catalyst in 1 mL of *i*PrOH) was injected. An aliquot of the mixture (0.1 mL) was quenched with 1 mL of H_2O and extracted with diethyl ether (1 mL). The product ratio was determined by GC analysis.

Single crystal X-ray structure determination of compounds 1-Cl and 5-Cl

General. Crystallographic data are presented in the electronic supplementary information, ESI.† Preliminary examination and data collection were carried out on an area detecting system (**1-Cl**: Xcalibur™3; **5-Cl**: APEX II) at the window of sealed tubes and graphite monochromated radiation **1-Cl**: Mo Kα (λ = 0.71073 Å) and **5-Cl**: Cu Kα (λ = 1.54180 Å). Data collections were performed at 153 K (**1-Cl**) and 173 K (**5-Cl**). Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, for latent decay and absorption effects. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atom positions were calculated in ideal positions (riding model). Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with SHELXL-97 weighting scheme. The final residual electron density maps showed no remarkable features.

Specific details. **1-Cl**: formula: $C_{13}H_{22}ClIrN_2$; M_r= 434.00; crystal system: orthorhombic; space group $P2_12_12_1$ (no. 19); a = 7.2573(1); b = 12.3428(1); c = 15.7279(1) Å; V = 1408.83(2) Å^3; Z = 4; data collected: 34 211; independent data [$I_o > 2\sigma(I_o)$/all data/R_{int}]: 2559/2576/0.030; data/restraints/parameters: 2576/0/157; $R1$ [$I_o > 2\sigma(I_o)$/all data]: 0.0149/0.0151; $wR2$ [$I_o > 2\sigma(I_o)$/all data]: 0.0373/0.0374. The correct enantiomer is proved by Flack's parameter ε = –0.016(8). Small extinction effects were corrected with the SHELXL-97 procedure and x = 0.0016(1). **5-Cl**: formula: $C_{19}H_{32}ClIrN_2$; M_r= 516.14; crystal system: monoclinic; space group $P2_1/c$ (no. 14); a = 11.1962(4); b = 19.4417(6); c = 17.7586(6) Å; β = 91.4342(15); V = 3864.4(2) Å^3; Z = 8; data collected: 47 684; independent data [$I_o > 2\sigma(I_o)$/all data/R_{int}]: 6636/6727/0.127; data/restraints/parameters: 6727/0/428; $R1$ [$I_o > 2\sigma(I_o)$/all data]: 0.0425/0.0430; $wR2$ [$I_o > 2\sigma(I_o)$/all data]: 0.1116/0.1120. In the unit cell two crystallographic independent molecules **A** and **B** were found. Small extinction effects were corrected with the SHELXL-97 procedure and x = 0.00057(3).

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References

1 (*a*) B. Cornils and W. A. Herrmann, *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd edn, VCH-Wiley, Weinheim, 2002, 204; (*b*) E. A. Braude and R. P. Linstead, *J. Chem. Soc.*, 1954, 3544.
2 B. Cornils, W. A. Herrmann, R. Schlögl, C.-H. Wong, *Catalysis from A to Z*, 2nd edn, Wiley-VCH, Weinheim, 2003, 780.
3 (*a*) J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, *J. Chem. Soc. A*, 1966, **12**, 1711; (*b*) W. A. Herrmann and B. Cornils, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 1049.
4 (*a*) R. H. Crabtree, H. Felkin and G. E. Morris, *J. Organomet. Chem.*, 1977, **135**, 205; (*b*) R. H. Crabtree and G. E. Morris, *J. Organomet. Chem.*, 1977, **135**, 395; (*c*) R. H. Crabtree, *Acc. Chem. Res.*, 1979, **12**, 331; (*d*) R. H. Crabtree, H. Felkin, T. Fillebeen-Khan and G. E. Morris, *J. Organomet. Chem.*, 1979, **168**, 183.
5 Exemplary work on transfer hydrogenation catalysis: (*a*) D. Gnanamgari, E. L. O. Sauer, N. D. Schley, C. Butler, C. D. Incarvito and R. H. Crabtree, *Organometallics*, 2009, **28**(1), 321; (*b*) J. Liu, X. Wu, J. A. Iggo and J. Xiao, *Coord. Chem. Rev.*, 2008, **252**, 792; (*c*) X. Wu, X. Li, A. Zanotti-Gerosa, A. Pettman, J. Liu, A. James Mills and J. Xiao, *Chem. Eur. J.*, 2008, **14**, 2209; (*d*) W. Baratta, M. Bosco, G. Chelucci, A. Del Zotto, K. Siega, M. Toniutti, E. Zangrando and P. Rigo, *Organometallics*, 2006, **25**, 4611; (*e*) J. R. Miecznikowsi and R. H. Crabtree, *Polyhedron*, 2004, **23**(17), 2857; (*f*) E. Peris and R. H. Crabtree, *Coord. Chem. Rev.*, 2004, **248**, 2239; (*g*) C. Saluzzo and M. Lemaire, *Adv. Synth. Catal.*, 2002, **344**(9), 915; (*h*) M. Albrecht, J. R. Miecznikowski, A. Samuel, J. W. Faller and R. H. Crabtree, *Organometallics*, 2002, **1**(17), 3596; (*i*) M. Yamakawa, H. Ito and R. Noyori, *J. Am. Chem. Soc.*, 2000, **122**, 1466; (*j*) R. Noyori and S. Hashiguchi, *Acc. Chem. Res.*, 1997, **30**(2), 97.
6 (*a*) D. J. Cardin, B. Cetinkaya and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545; (*b*) J. E. Hill and T. A. Nile, *J. Organomet. Chem.*, 1977, **137**, 293; (*c*) M. F. Lappert and R. I. K. Maskell, *J. Organomet. Chem.*, 1984, **264**, 217; (*d*) M. Sholl, S. Ding, C. W. Lee and R. H. Grubbs, *Org. Lett.*, 1991, **1**, 953; (*e*) W. A. Herrmann and C. Köcher, *Angew. Chem. Int. Ed.*, 1997, **36**, 2162; (*f*) M. G. Gardiner, W. A. Herrmann, C. P. Reisinger, J. Schwarz and M. Spiegler, *J. Organomet. Chem.*, 1999, **572**, 239; (*g*) D. Bourissou, O. Guerret, F. P. Gabbai and G. Bertrand, *Chem. Rev.*,

2000, **100**, 39; (*h*) M. Mühlhofer, T. Strassner and W. A. Herrmann, *Angew. Chem. Int. Ed.*, 2002, **41**, 1745; (*i*) W. A. Herrmann, *Angew. Chem. Int. Ed.*, 2002, **41**, 1290; (*j*) *N-Heterocyclic Carbenes in Synthesis*, ed. S. P. Nolan, Wiley-VCH, 2006; (*k*) *N-Heterocyclic Carbenes in Transition Metal Catalysis (Topics in Organometallic Chemistry)*, ed. F. Glorius, Springer, Berlin, Heidelberg, 2007; (*l*) F. E. Hahn and M. C. Jahnke, *Angew. Chem. Int. Ed.*, 2008, **47**, 3122.

7 (*a*) J. R. Miecznikowski and R. H. Crabtree, *Organometallics*, 2004, **23**, 629; (*b*) E. Mas-Marza, M. Sanau and E. Peris, *Inorg. Chem.*, 2005, **44**, 9961.

8 (*a*) D. Gnanamgari, A. Moores, E. Rajaseelan and R. H. Crabtree, *Organometallics*, 2007, **26**, 1226; (*b*) F. E. Hahn, C. Holtgrewe, T. Pape, M. Martin, E. Sola and L. A. Oro, *Organometallics*, 2005, **24**, 2203; (*c*) H. Türkmen, T. Pape, F. E. Hahn and B. Cetinkaya, *Organometallics*, 2008, **27**, 571; (*d*) H. Türkmen, T. Pape, F. E. Hahn and B. Cetinkaya, *Eur. J. Inorg. Chem.*, 2008, **34**, 5418.

9 B. Cetinkaya, P. Dixneuf and M. F. Lappert, *Chem. Commun.*, 1973, 206.

10 (*a*) W. A. Herrmann, M. Elison, J. Fischer, C. Köcher and G. R. J. Artus, *Chem. Eur. J.*, 1996, **2**, 772; (*b*) K. Denk, P. Sirsch and W. A. Herrmann, *J. Organomet. Chem.*, 2002, **649**, 219; (*c*) J. Schütz and W. A. Herrmann, *J. Organomet. Chem.*, 2004, **689**, 2995; (*d*) M. Prinz, L. F. Veiros, M. J. Calhorda, C. C. Romao, E. Herdtweck, F. E. Kühn and W. A. Herrmann, *J. Organomet. Chem.*, 2006, **691**, 4446.

11 C. Köcher and W. A. Herrmann, *J. Organomet. Chem.*, 1997, **532**, 265.

12 (*a*) A. M. Voutchkova, L. N. Appelhans, A. R. Chianese and R. H. Crabtree, *J. Am. Chem. Soc.*, 2005, **127**, 17624; (*b*) P. J. Fraser, W. R. Roper and F. G. A. Stone, *Dalton Trans.*, 1974, 760; (*c*) S. Leuthhäußer, D. Schwarz and H. Plenio, *Chem. Eur. J.*, 2007, **13**, 7195; (*d*) A. P. Blum, T. Ritter and R. H. Grubbs, *Organometallics*, 2007, **26**, 2122; (*e*) T. Chen, X.-G. Liu and M. Shi, *Tetrahedron*, 2007, **63**, 4874; (*f*) A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller and R. H. Crabtree, *Organometallics*, 2003, **22**, 1663; (*g*) L. D. Vazquez-Serrano, B. T. Owens and J. M. Buriak, *Inorg. Chim. Acta*, 2006, **359**, 2786; (*h*) S. Burling, M. F. Mahon, S. P. Reade and M. K. Whittlesey, *Organometallics*, 2006, **25**, 3761; (*i*) R. A. Kelly, H. Clavier, S. Giudice, N. M. Scott, E. D. Stevens, J. Bordner, C. D. Hoff, L. Cavallo and S. P. Nolan, *Organometallics*, 2008, **27**, 202.

13 (*a*) M. Viciano, E. Mas-Marza, M. Sanau and E. Peris, *Organometallics*, 2006, **25**, 3063; (*b*) M. Viciano, M. Poyatos, M. Sanau, E. Peris, A. Rossin, G. Ujaque and A. Lledos, *Organometallics*, 2006, **25**, 1120.

14 (*a*) W. A. Herrmann, J. Schütz, G. D. Frey and E. Herdtweck, *Organometallics*, 2006, **25**, 2437; (*b*) G. D. Frey, C. F. Rentzsch, D. v. Preysing, T. Scherg, M. Mühlhofer, E. Herdtweck and W. A. Herrmann, *J. Organomet. Chem.*, 2006, **691**, 5725.

15 K. Brandenburg, *Diamond, Version 3.1d*, Crystal Impact GbR, Bonn, Germany, 2006.

16 B. Cornils, W. A. Herrmann, M. Muhler and C.-H. Wong, *Catalysis from A to Z*, 3rd completely revised and enlarged edition, Wiley-VCH, Weinheim, 2007, 1462.

17 R. Spogliarich, A. Tencich, J. Kaspar and M. Graziani, *J. Organomet. Chem.*, 1982, **240**, 453.

18 A. C. Hillier, H. M. Lee, E. D. Stevens and S. P. Nolan, *Organometallics*, 2001, **20**, 4246.

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

20 M. Albrecht, J. R. Miecznikowski, A. Samuel, J. W. Faller and R. H. Crabtree, *Organometallics*, 2002, **21**(17), 3596.

21 B. L. Benac, E. M. Burgess and A. J. Arduengo III, *Org. Synth.*, 1986, **64**, 92.

22 W. A. Herrmann, C. Köcher and L. Goossen, *PCT Int. Appl.*, 1997, WO 9734875.

23 F. Hanasaka, K. Fujita and R. Yamaguchi, *Organometallics*, 2005, **24**(14), l3422.

