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Donor-Functionalised Expanded Ring N-Heterocyclic Carbenes: Highly Effective Ligands in Ir-Catalysed Transfer Hydrogenation

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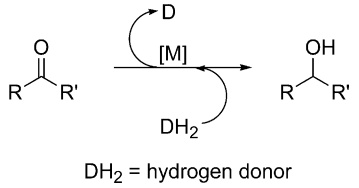
The performances of a number of Rh^I and Ir^I complexes of type [M(NHC)(COD)Cl] in the transfer hydrogenation of ketones were tested under a variety of reaction conditions, and with a variety of substrates, allowing comparison of Rh- and Ir-NHC complexes, and also comparison of the influence of the NHC ligand on catalytic performance. Notably, of the Rh^I and Ir^I complexes with symmetrically substituted NHCs only those bearing cyclohexyl substituents were active, with Rh^I complexes of saturated 5-, 6- and 7-NHCs with N-Mes substituents, [Rh(5,6,7-Mes)(COD)Cl], showing no activity in transfer hydrogenation under the test conditions. Rh^I and Ir^I complexes of unsymmetrical *o*-methoxyphenyl donor-functionalised NHCs (df-NHC) with differing carbene ring sizes were also tested in transfer hydrogenations, with the Rh^I complexes displaying no catalytic activity. However, the corresponding df-NHC Ir^I complexes were found to be extremely effective catalysts. Catalyst tests also demonstrated the excellent stability of these complexes.

Introduction

N-Heterocyclic carbenes (NHCs) in all their forms, are widely studied, and many examples have proved to be important ligands in catalysis.[1] We recently become interested in developing "expanded" or large-ring NHCs, i.e. NHCs with ring sizes of six and above.[2] We reported the synthesis of large-ring NHCs, and their complexes with Ag, Rh and Ir; studies also included examples of novel donor-functionalised 6- and 7-membered NHCs, (both symmetrically substituted, and unsymmetrical mono-substituted ligands).[3–6] The large ring NHCs are very basic and show unique structural characteristics; the enlarged NCN angles (> 120° in some cases), cause the N-substituents to twist towards the metal centre, providing steric protection at the active site and ^{13}C NMR spectroscopic data indicates that the $C_{carbene}$ shift is at extremely low field (as low as δ = 260 ppm for 7-membered ring carbenes).[4,5] A number of novel examples of large-ring structures have also been described,[7] however, the study of such NHCs, and in particular their application in catalysis remains relatively limited.[8] Our recent studies examined the application of such ligands in Rh catalysed hydrogenation; it was evident that the large rings impart improved stability on the catalysts, and relatively efficient, long-lived catalysts were generated.[6] It is now timely to investigate other catalytic processes using these novel ligands. The reaction of interest here is transfer hydrogenation.

The reduction of ketones or aldehydes is an important reaction in organic synthesis. One of the most commonly used methods is transfer hydrogenation (Scheme 1); it is a valuable, atom efficient reaction, and compared with conventional hydrogenation, using molecular hydrogen, transfer hydrogenation offers a safer, more cost effective and simpler experimental procedure. A wide number of alcohols and other reagents are available as a source of hydrogen, and mild reaction conditions are used.[9] Research in this area initially focused on Ru complexes as catalysts.[10] More recently, Crabtree and co-workers,[11] and other groups,[12] explored the efficiency of N-heterocyclic carbenes as ligands in transfer hydrogenation.



Scheme 1. Schematic representation of a transfer hydrogenation.

The reaction mechanism could involve either a mono- or dihydrido intermediate. However, theoretical studies on rhodium-catalysed transfer hydrogenations, in which the active species is a Rh-COD-diamine complex, concluded that the mechanism takes place via a monohydride route in a stepwise hydrogen transfer (Scheme 2).[13]

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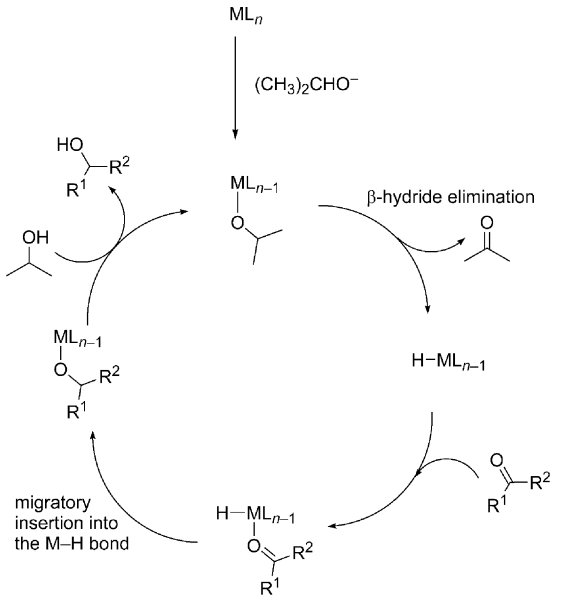


Scheme 2. Generic catalytic cycle for the reduction of ketones via the monohydride route.

The activity of rhodium and iridium NHC complexes for catalytic transfer hydrogenation was found to dramatically improve using chelating bis-carbenes as ligands. Peris, Crabtree and co-workers synthesized Rh^{III} bis-carbene complexes [Rh^{III}(biscarbene)(OAc)I_2] and found them to be effective catalysts for transfer hydrogenation.[11a] This was closely followed by a similar study of related Ir^{III} complexes.[11b,11c] In contrast to phosphane based catalysts, Ir-carbene complexes are more active than their Rh analogues.[14] Recent studies have also investigated enantioselective transfer hydrogenation using chiral NHC complexes with limited success to date.[15] At best, *ee* values have been modest and more work is necessary to achieve useful performance.

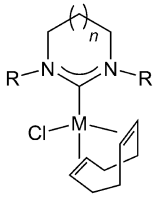
Donor-functionalised NHC's (df-NHC) have played an important role in organometallic chemistry and catalysis.[1r] Tridentate (pincer type) and bidentate ligands can provide unique opportunities due to the extra stability they impart to intermediates in a catalytic reaction. The use of large ring df-NHCs as ligands in catalysis is largely unexplored. One publication reported the synthesis of functionalised-tridentate, difurfuryl- and dithiophenylmethyl-substituted 6- and 7-membered ring NHC salts.[8k] The salts were tested in situ, with $Pd(OAc)_2$ in Heck coupling reactions, with modest activity. No free carbenes and no metal complexes were reported. We recently described the synthesis of pyridine- and *o*-methoxyphenyl-functionalised 6- and 7-membered NHCs and their Rh and Ir complexes.[6] The *o*-methoxyphenyl-functionalised NHC complexes were tested in catalytic hydrogenation and found to be surprisingly effective; the large rings and *o*-methoxy substituent appear to impart high stability.[6] In this paper we focus on the catalytic performance of selected expanded ring, and functionalised expanded ring-NHC complexes of rhodium and iridium in transfer hydrogenation. Examples of the large ring df-NHCs demonstrate excellent performance, and as reported above the *o*-methoxy substituent seemed to provide particular benefits.

Results and Discussion

Synthesis of Salts and Complexes

N-Substituted aryl and alkyl heterocyclic salts have been prepared in high yields via the amidine route, as previously reported.[3,5] The salts were fully characterised by NMR and in some cases by X-ray crystallography.[6]

The synthesis of complexes of expanded ring NHCs, including Rh and Ir complexes, **12**–**17** [M(*n*-R)(COD)Cl] (Scheme 3; *n* = ring size and R is the NHC N-substituent) has been described previously.[2–6] For simplicity, we have used the following notation: 5-membered ring carbenes with mesitylene groups on the ring Ns are designated (5-Mes) and similarly 6- and 7-membered systems are designated (6-R) and (7-R) respectively; for asymmetrically substituted rings the designation is *n*-R,R′. For example, in complexes of the type [M(NHC)(COD)Cl] in which one N has a *o*-methoxyphenyl-substituent and the other N a mesitylene substituent, we use the form [M(*n*-*o*-MeOPh,Mes)-(COD)Cl] to describe the complex. Synthesis of complexes involved either the addition of preformed free carbene to the appropriate starting complex, or an in situ method, in which the heterocyclic salt was first treated with base followed by addition of metal precursor complex. Methoxy-functionalised systems **16**–**17** were prepared by the in situ route.

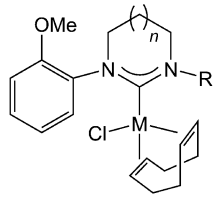


M = Rh

12 *n* = 0, R = Mes (5-Mes)
13 *n* = 1, R = Mes (6-Mes)
14a *n* = 2, R = Mes (7-Mes)
14b *n* = 2, R = Cy (7-Cy)

M = Ir

15 *n* = 2, R = Cy (7-Cy)



16a–**e** M = Rh

n = 1, R = Mes (**a**), DiPP (**b**)
n = 2, R = Mes (**c**), DiPP (**d**)
n = 1, R = MeOPh (**e**)

17a–**d** M = Ir

n = 1, R = Mes (**a**), DiPP (**b**)
n = 2, R = Mes (**c**), DiPP (**d**)

Scheme 3. Rh and Ir complexes of large-ring NHCs synthesised in this study.

Ketone Transfer Hydrogenation Catalysis

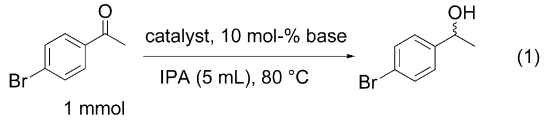
The performances of rhodium(I) and iridium(I) complexes of type [M(NHC)(COD)Cl] were tested under a variety of reaction conditions, and with a variety of substrates, allowing comparison of Rh and Ir complexes, and also comparison of the influence of the NHC ligand on catalytic performance.

Initial catalytic testing was undertaken with the Rh and Ir complexes, [M(7-Cy)(COD)Cl], **14b** and **15** respectively (Table 1) for the transfer hydrogenation of 4-bromoacetophenone to the corresponding alcohol using *i*PrOH with potassium *tert*-butoxide as the base [Equation (1)]. The iridium complex [Ir(7-Cy)(COD)Cl], **15**, shows a higher activity than its rhodium analogue, **14b**, as has been previously reported for other carbene based catalysts. Interestingly, rhodium(I) complexes of saturated 5-, 6- and 7-NHCs with N-Mes substituents, [Rh(5,6,7-Mes)(COD)Cl], show no activity in transfer hydrogenation under the test conditions. The significant effect of the N-substituents on activity is consistent with a hydride mechanism.[16] The mechanism entails substrate coordination prior to its reduction by the hydride and hence steric properties of the NHC will have a major impact on selectivity and reactivity of the resultant catalyst. Complexes of 7-Mes are significantly more sterically hindered than their Cy counterparts, and in the case of the 6- and 7-membered rings, these effects will be further accentuated by the intrusion of the Mes groups into the reaction sphere of the metal centre.[5] Evidence for this is the observation that the NHC ligand in complex [Rh(7-Cy)$(CO)_2$Cl] is able to rotate at ambient temperature, whereas 7-Mes does not.

Table 1. Catalytic testing of Rh and Ir complexes of symmetrically substituted 5-, 6- and 7-membered ring NHCs.

Catalyst (mol-%)[a]	Conversion [%]	TON
15 Ir(7-Cy)(COD)Cl (1)	100	100
15 Ir(7-Cy)(COD)Cl (0.1)	61	610
15 Ir(7-Cy)(COD)Cl (0.01)	54	5400
15 Ir(7-Cy)(COD)Cl (0.001)	11	11000
14b Rh(7-Cy)(COD)Cl (1)	63	63
14b Rh(7-Cy)(COD)Cl (0.1)	47	470
14b Rh(7-Cy)(COD)Cl (0.01)	26	2600
Rh(5,6,7-Mes)(COD)Cl (1)[b]	0	–

[a] Reaction conditions: t = 80 °C, 24 h, 5 mL of *i*PrOH per 1 mmol of 4-bromoacetophenone; 10 mol-% *t*BuOK, conversion determined by ^{1}H NMR spectroscopy. [b] *t*BuOK or K[HMDS].



The time dependence for transfer hydrogenation of 4-bromoacetophenone was monitored, using 0.1 mol-% **15** or **14b** as catalysts, with *t*BuOK as base, and is shown in Figure 1. These catalysts, particularly the Rh complex, show only modest activity, and the plots indicate a delay, or induction period before initiation of the catalytic process. TONs and TOFs obtained after 3 h are, 490 and 163 h^{-1} for **15** and 190 and 63 h^{-1} for **14b**. Rate constants were determined for each of the catalysts (the plots are provided in the Supporting Information); for the iridium catalyst the plot is a straight line indicating pseudo-first-order behaviour. The corresponding plot for the rhodium catalyst deviates from a straight line at long reaction times, but data collected during the first 180 min does fit a straight line, suggesting a loss of catalyst activity at longer reaction times due to decomposition of the catalyst (a suspension of rhodium black is observed after 24 h). For the complex [Ir(**7-Cy**)(COD)Cl] $k = 0.0032 \pm 0.0001$ min^{-1}, and for [Rh(**7-Cy**)(COD)Cl] $k = 0.0004 \pm 0.0001$ min^{-1}.

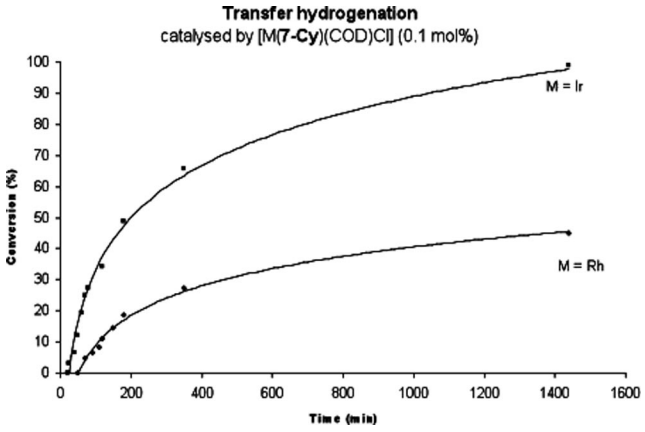


Figure 1. Time dependence for the transfer hydrogenation of 4-bromoacetophenone using 0.1 mol-% of [Ir(**7-Cy**)(COD)Cl] and [Rh(**7-Cy**)(COD)Cl] at 80 °C with *t*BuOK as base.

Following these initial studies, we examined catalytic transfer hydrogenation of 4-bromoacetophenone with Ir complexes of *o*-methoxyphenyl-functionalised NHCs, **17a**–**d**. 2-Propanol was employed as the hydrogen source and *t*BuOK or KOH as the base. Significantly improved performances are noted for these systems, particularly for **17c**, [Ir(7-OMe,Mes)(COD)Cl], and **17d** [Ir(**7-**OMe,DIPP)-(COD)Cl]. Results are presented in Table 2. Interestingly, the Rh complexes **16a**–**d** showed no activity (**16e** was not tested).

Table 2. Transfer hydrogenation of 4-bromoacetophenone with Ir complexes of *o*-methoxyphenyl-functionalised NHCs.

Catalyst (mol-%)[a]	Concentration [mol-%]	Conversion [%][b]	TON
17a Ir(6-MeOPh/Mes)(COD)Cl	1	100	100
	0.1	100	1000
	0.01	71	7100
17b Ir(6-MeOPh/DIPP)(COD)Cl	1	100	100
	0.1	100	1000
	0.01	73	7300
17c Ir(7-MeOPh/Mes)(COD)Cl	1	100	100
	0.1	100	1000
	0.01	96	9600
17d Ir(7-MeOPh/DIPP)(COD)Cl	1	100	100
	0.1	100	1000
	0.01	97	9700

[a] Reaction conditions: 10 mol-% base, t = 80 °C, 24 h, 5 mL of *i*PrOH per 1 mmol of substrate. [b] Conversion calculated by ^{1}H NMR spectroscopy.

Conversion vs. time plots for the conversion of 4-bromoacetophenone using 1 mol-% of complexes **17c** and **17d** as pre-catalysts are shown in parts a and b of Figure 2. The reaction was monitored by removing aliquots (0.1 mL) from the reaction mixture at 5 min intervals and the % conversion determined. A conversion vs. time plot using complex **17b** is also provided in the Supporting Information.

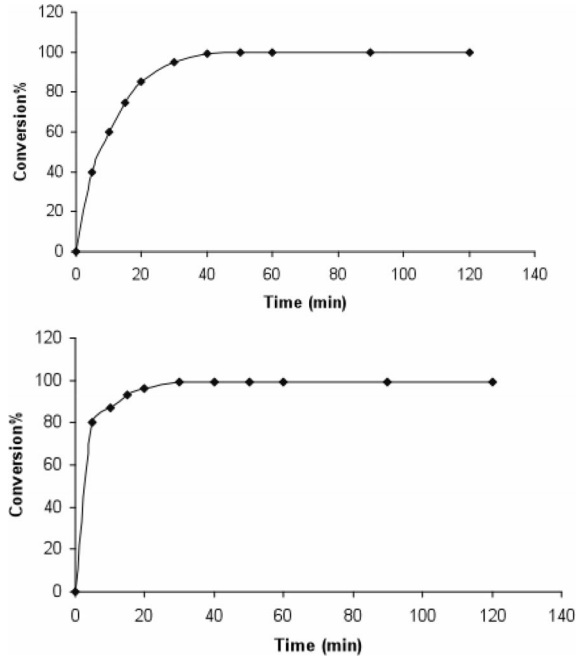


Figure 2. Conversion verses time plots for transfer hydrogenation of 4-bromoacetophenone using 1 mol-% of **17c** and **17d** as catalysts.

As shown in Figure 2, both catalysts **17c** and **17d** appear to be very efficient in transfer hydrogenation of 4-bromoacetophenone to 1-(4-bromobenzene)ethanol (there is no indication of an induction period and quantitative conversion is achieved in less than 30 min). Catalyst **17d** (80% conversion within less than 5 min) shows notably better performance than **17c**, which took 20 min for a similar conversion. Crabtree and co-workers[11b] have suggested that TOF_{50} (the TOF at 50% conversion) is a useful way to define catalyst activity; using this approach, for complex **17c** (Figure 2) a value of 400 h^{-1} is obtained. For **17d** the line is very steep at 50% conversion (and the first reading was only taken after 5 min) therefore, the error is large, however, 50% conversion is conservatively estimated to occur around 2 min, giving a TOF_{50} of 1500 h^{-1}. Considering the curve of the line for **17d** following 80% conversion, this Figure is likely to be a significant underestimate – 50% conversion probably occurs after seconds.

The strong donor properties, and steric demands of the large ring NHCs, resulting from their very large NCN angles, may play an important role in the improved performance of these systems. Complex **17d** is more sterically hindered than **17c**, because of the presence of the bulky DIPP moiety, which appears to lead to an improvement in activity. In addition, a weak interaction between the *o*-methoxy substituent on the ligand and the metal centre may also help to stabilise the highly coordinatively unsaturated intermediate, possibly generated during catalysis. The proposed formation of an unsaturated intermediate is supported by the low activity of the biscarbonyl derivatives towards catalytic transfer hydrogenation; carbonyl ligands are more tightly bound to the metal centre than COD. In addition, Herrmann and co-workers have suggested that sterically demanding substrates (such as acetophenone) may improve reaction rates by helping stabilise the transition state.[17] Their studies also showed that increasing donor strength of the NHC leads to a shorter induction period and higher initial activity. These observations are consistent with results reported here. Overall, the catalytic performance of these large ring *o*-methoxyphenyl-functionalised NHC-Ir complexes, although not optimised in terms of catalyst precursor or reaction conditions, compare very favourably with the best systems previously reported for 5-membered ring systems.[11b,17–19]

To test catalyst performance at lower temperatures, the transfer hydrogenation of 4-bromoacetophenone was determined at temperatures from 20–80 °C (conversions were measured by NMR). It was found that with *t*BuOK as base, and using either **17c** or **17d** as catalyst, a minimum temperature of 40–50 °C is required to give quantitative yields in 24 h. With KOH as base conversions were slightly lower and a temperature of > 60 °C is required for complete conversion in the 24 h time frame. Full results are reported in the Supporting Information.

Complex **17d** was also used to test the lifetime/stability of these catalyst systems. A catalytic run was initiated using standard conditions but after 20 min operating time, when > 90% conversion had been obtained, an additional 1 mmol of substrate was added to the solution and the reaction monitored for a further 20 min, after which time a third aliquot of substrate was added and the reaction again monitored. The results are shown in Figure 3. It is clear that the catalyst maintained high activity during the entire experiment despite decreasing concentration of catalyst (due to loss of small amounts of catalyst as aliquots were taken for analysis), and increasing concentration of product in the reaction solution (initial conc. of catalyst: 1 mol-%; final conc.: less than 0.3 mol-%). There was no evidence of catalyst decomposition.

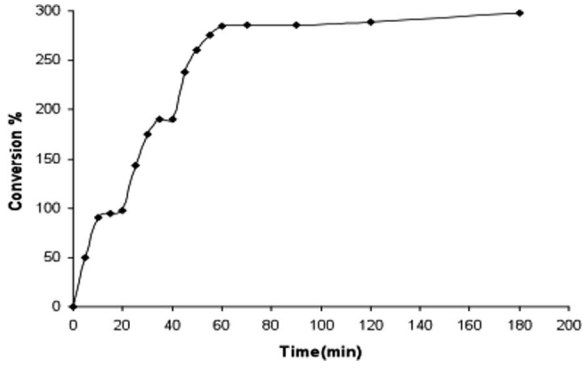


Figure 3. Catalytic conditions: 3.0 mmol 4-bromoacetophenone, added in three separate stages; 0.01 mmol catalyst **17d**; 0.1 mmol *t*BuOK; 5 mL of IPA; 80 °C.

To further explore the effectiveness of these catalysts other substrate, 4-methylacetophenone, acetophenone and cyclohexanone, were also investigated under identical reaction conditions; the results are summarised in Table 3.

Table 3. Conversion of alternative substrate using complexes **17c** and **17d**.

Catalyst[a] [mol-%]	Substrate/concentration [mol-%]	Conversion [%]
17d	4-methylacetophenone	
	1	100
	0.1	100
	0.01	75
17c	acetophenone	
	1	100
	0.1	100
	0.01	82
17d	acetophenone	
	1	100
	0.1	100
	0.01	86
17c	cyclohexanone	
	1	100
	0.1	100
	0.01	98
17d	cyclohexanone	
	1	100
	0.1	100
	0.01	100

[a] Catalytic conditions: ketone (1.0 mmol); *t*BuOK (0.1 mmol); IPA (5 mL); 80 °C; 24 h. Conversion determined by NMR analysis.

A preliminary examination of the effect of base (*t*BuOK or KOH) on the reaction was also undertaken. With 4-bromoacetophenone and cyclohexanone as substrate there was no discernible difference in conversion irrespective of the base used. However, in the conversion of acetophenone at low catalyst loadings (0.01 mol-%), *t*BuOK proved to be marginally more effective (Table 4).

Table 4. Comparison of *t*BuOK and KOH as base using complexes **17c** and **17d**.

Catalyst[a] [mol-%]	Base	Conversion [%]
17c (0.01)	*t*BuOK	83
17c (0.01)	KOH	80
17d (0.01)	*t*BuOK	86
17d (0.01)	KOH	81

[a] Catalytic conditions: acetophenone (1.0 mmol); base (0.1 mmol); IPA (5 mL); 80 °C; 24 h. Conversion determined by NMR analysis.

Conclusions

Examples of expanded-ring NHC complexes of Ir have been examined in the catalytic transfer hydrogenation of a number of substrate ketones. In particular Ir complexes containing 7-membered ring NHCs [Ir(7-*o*-MeOPh,Mes)(COD)Cl], [Ir(7-*o*-MeOPh,DIPP)(COD)Cl] were found to be extremely effective. These catalyst systems showed good activity for the range of substrate tested and also demonstrated excellent stability. These results suggest that the sterically demanding, large-ring NHCs may offer unique opportunities in selected catalytic reactions, in which coordinative unsaturation is important and in which reductive elimination does not play a key role.

Experimental Section

General Remarks: All manipulations were performed using standard Schlenk techniques under an argon atmosphere, except where otherwise noted. Complexes $[Rh(COD)Cl]_2$, $[Ir(COD)Cl]_2$ were synthesised according to literature methods.[20] NHC salts and the Rh and Ir complexes were prepared as previously reported.[6] Solvents of analytical grade were freshly distilled from sodium/benzophenone (thf, hexane) or from calcium hydride (CH_2Cl_2) or dried using a Braun SPS system (hexane, CH_2Cl_2) or a Vacuum Atmospheres recirculating SPS system (thf). Deuterated solvents for NMR measurements were distilled from the appropriate drying agents under N_2 immediately prior to use, following standard literature methods. Air-sensitive compounds were stored and weighed in a glovebox. All reagents [1,3-dibromopropane, 1,4-diiodobutane, 2-aminopyridine, *o*-anisidine, 2,6-dimethylaniline, 2,6-diisopropylaniline, triethyl orthoformate, sodium tetrafluoroborate, and potassium bis(trimethylsilyl)amide] were used as received. ^1H and ^{13}C NMR spectra were obtained on Bruker Advance AMX 400, 500 or Jeol Eclipse 300 spectrometers. Chemical shifts (δ) were expressed in ppm downfield from tetramethylsilane using the residual proton as an internal standard ($CDCl_3$, ^1H: 7.26 ppm and ^{13}C: 77.0 ppm; $[D_6]$benzene ^1H: 7.15 ppm and ^{13}C: 128.0 ppm). Coupling constants J are expressed in Hz. HRMS were obtained on a Waters LCT Premier XE instrument and are reported as m/z (%). Infrared spectra were recorded using a JASCO FT/IR-660 Plus spectrometer and analysed in solution (dichloromethane).

General Protocol for Catalytic Transfer Hydrogenation: The catalyst precursor was dissolved in a solution of *t*BuOK (0.01 mmol) in 2-propanol (5 mL) and 4-bromoacetophenone (1 mmol) in a Schlenk tube. The solution was heated to 353 K for 24 h, volatile components were evaporated and the final conversions calculated by using ^1H NMR spectra.

The reaction progress was monitored by GC–MS analysis in order to calculate the time dependence of the transfer hydrogenation of 4-bromoacetophenone. Aliquotes of 0.1 mL were taken were taken every 5 min for the first 30 min, every 10 min the next 90 min, every 30 min for the next hour, and finally another two samples were taken after 350 min and a final one after 24 h. The samples were filtered through a short pad of silica, and the silica was washed with DCM.

Description of GC/MS Analysis: Yields and substrate identities were determined by GC-MS analysis of reaction mixtures using an Agilent Technologies 6890N GC system with an Agilent Technologies 5973 inert MS detector with MSD. Column: Agilent 190915-433 capillary, 0.25 mm × 30 m × 0.25 μm. Capillary: 30 m × 250 μm × 0.25 μm nominal. Initial temperature at 50 °C, held for 4 min, ramp 5 °C/minute next 100 °C, ramp 10 °C/minute next 240 °C hold for 15 min. The temperature of the injector and the detector were held at 240 °C. The retention times for analytes (in minutes); for 4-bromoacetophenome: 18.3, for 1-(4-bromophenyl)ethanol: 18.7.

Supporting Information (see also the footnote on the first page of this article): Graphs for the rate constant (k) determinations and reaction profile plots.

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