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Efficient transfer hydrogenation of ketones in the presence of ruthenium *N*-heterocyclic carbene catalysts

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Abstract

Novel ruthenium carbene complexes have been *in situ* generated and tested for the transfer hydrogenation of ketones. Applying $Ru(cod)(methylallyl)_2$ in the presence of imidazolium salts in 2-propanol and sodium-2-propanolate as base, turnover frequencies up to 346 h^{-1} have been obtained for reduction of acetophenone. A comparative study involving ruthenium carbene and ruthenium phosphine complexes demonstrated the higher activity of ruthenium carbene complexes.

Keywords: Ruthenium; Homogeneous catalysis; Transfer hydrogenation; *N*-heterocyclic carbenes; Ketones

1. Introduction

The preparation of alcohols has become an important field of activity for transition metal catalyzed reactions [1]. Within the different catalytic approaches developed, for instance addition of organometallic reagents to carbonyl compounds, hydroxylation of olefins, functionalization reactions of epoxides, the hydrogenation of ketones or aldehydes is the most powerful tool with respect to industrial applications. In particular, transfer hydrogenations represent a potent strategy, because of high atom efficiency, no need of pressure, and economic as well as environmental advantages [2]. In more detail, a broad scope of alcohols is accessible by transfer hydrogenation using non-toxic hydrogen donors under mild reaction conditions in the presence of various metal catalysts, such as Ir, Rh or Ru [2d]. Noteworthy, a prerequisite for achieving high activity and selectivity is the fine tuning of the metal catalyst by introduction of ligands. So far the development of new ligands for catalytic reductions focused predominantly on phosphines and amines.

More recently carbene ligands found increasing interest for exploiting new catalytic reactions [3]. Stable *N*-heterocyclic carbenes (NHC) were first introduced in the early 1990's by Arduengo et al. [4]. Since the mid 1990's Herrmann et al. [5] and then the groups of Bertrand [6], Blechert [7], Cavell [8], Fürstner [9]. Glorius [10], Grubbs [11], Nolan [12] and others [13] demonstrated the catalytic potential of NHC metal complexes. In this context we reported that palladium carbene complexes are excellent catalysts for different coupling reactions of aryl halides and telomerizations [14].

With regard to transfer hydrogenations different carbene or carbene-phosphine-systems containing Rh [15], Ir [15,16], Ru [17] and Ni [18] have been reported. Excellent turnover frequencies up to 120,000 h^{-1} were reported by the groups of Baratta and Herrmann applying a ruthenium-carbene-phosphine-catalysts [19]. However, for reduction of a typical substrate, e.g. acetophenone, with phosphine-free ruthenium-carbene catalysts lower turnover frequencies (TOF 333 h^{-1}) [17e] were achieved in comparison to iridium (500 h^{-1}) [16c] and rhodium systems (583 h^{-1}) [15b]. Due to the economical benefit of ruthenium metal compared to rhodium or iridium and the advantages of phosphine-free systems, it is an important

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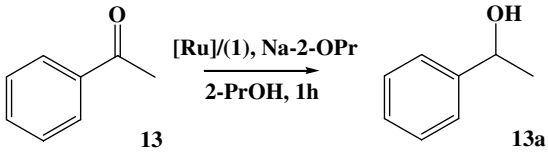
goal to search for more active ruthenium carbene catalysts. Herein, we report the application of novel *in situ* prepared ruthenium carbene catalysts in the reduction of different ketones.

2. Results and discussion

Based on our experience in the synthesis of carbene ligands and their application in homogeneous catalysis, we became interested in demonstrating the usefulness of carbene-complexes in ruthenium-catalyzed transfer hydrogenations [20]. From a practical point of view the application of *in situ* prepared catalysts has significant advantages. Thus, we used a small library of various imidazolium salts (Scheme 1, **1**–**12**) as carbene precursors. In exploratory experiments, 2-propanol-based transfer hydrogenation of acetophenone was examined. In order to ensure complete formation of the active catalyst a 2-propanol solution of 1 mol% ruthenium-source and 1 mol% 1,3-bis(2,6-di-*i*-propylphenyl)-imidazolium chloride (**1**) is stirred in the presence of 5 mol% sodium 2-propylate for 16 h at 65 °C.

Initial investigations showed a crucial effect on reactivity by using different ruthenium sources such as $[RuCl_2(C_6H_6)]_2$, $Ru_3(CO)_{12}$, and $Ru(cod)(methylallyl)_2$ in combination with imidazolium salt **1** (Table 1). Best conversion and yield are obtained for $Ru(cod)(methylallyl)_2$/**1** at 100 °C (Table 1, entry 8). Noteworthy, there is a significant temperature effect on the reaction rate (Table 1, entries 5–8).

Table 1
Screening of various ruthenium sources and yield-temperature dependency for the transfer hydrogenation of acetophenone (**13**)[a]



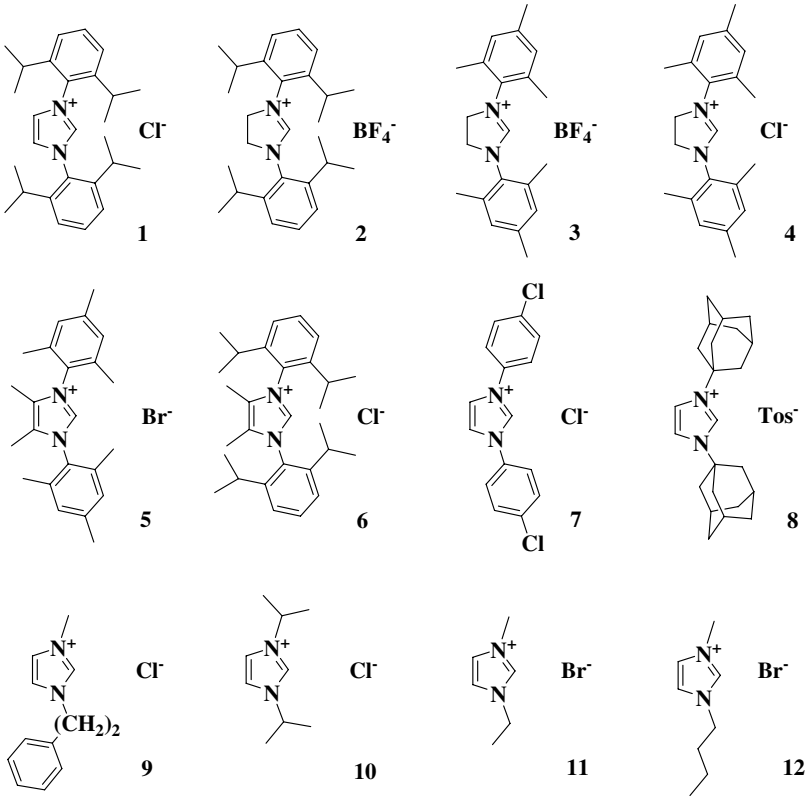
13 **13a**

Entry	Source	Temperature (°C)	Yield (%)[b]
1	$[RuCl_2(C_6H_6)]_2$	90	9
2	$[RuCl_2(C_6H_6)]_2$	100	80
3	$Ru_3(CO)_{12}$	90	40
4	$Ru_3(CO)_{12}$	100	16
5	$Ru(cod)(methylallyl)_2$	70	2
6	$Ru(cod)(methylallyl)_2$	80	43
7	$Ru(cod)(methylallyl)_2$	90	55
8	$Ru(cod)(methylallyl)_2$	100	>99

[a] *Reaction conditions*: *in situ* catalyst: 1.3×10^{-6} mol $Ru_3(CO)_{12}$, 1.9×10^{-6} mol $[RuCl_2(C_6H_6)]_2$ or 3.8×10^{-6} mol $Ru(cod)(methylallyl)_2$, 3.8×10^{-6} mol imidazolium salt **1** and 1.9×10^{-5} mol Na–2-OPr in 2.0 mL 2-propanol for 16 h at 65 °C, addition of 3.8×10^{-4} mol acetophenone (**13**), reaction 1 h at described temperature.

[b] Conversion is determined by GC analysis (50 m Lipodex E, 95–200 °C) with diglyme as internal standard.

It is well-known that transfer hydrogenations are sensitive to the nature of the base. Thus, the influence of sodium 2-propylate, potassium *tert*-butylate, potassium carbonate and sodium hydroxide on selectivity and conversion was investigated. In all cases excellent selectivity (>99%) is



Scheme 1. Selection of imidazolium salts.

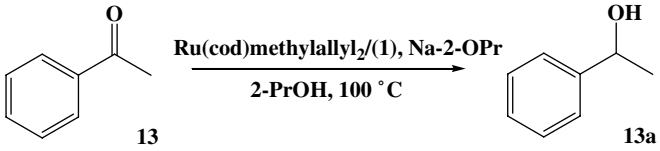
observed. Best conversion after 1 h at 100 °C are obtained in the presence of sodium 2-propylate (>99%) and potassium *tert*-butylate (95%). However, poor yields of 1-phenylethanol are achieved with potassium carbonate (53%). Interestingly, sodium hydroxide, one of the most common bases for transfer hydrogenation, induced only low conversion (62%). By increasing the amount of base a further acceleration of reaction rate is recorded, while no reaction occurred in the absence of base.

Next, the influence of the ligand concentration was investigated by variation of the metal to ligand-ratio. When increasing the equivalents of ligand per metal a negative effect on the reaction rate is observed (Table 2). We assume a catalyst deactivation by more than one carbene ligand, due to suppressing the metal hydride formation or blocking the active binding site for the substrate. However, 1 equiv. of ligand is necessary for achieving good conversion. Hence, transfer hydrogenations in absence of the carbene gave only moderate yield (Table 2, entry 1).

The stability of metal carbene complexes against moisture and oxygen has been documented [13]. Thus, the addition of water (10 mol%) to the reaction mixture decreased only slightly the conversion to 73% (TOF: 73 h^{-1}). Even in the presence of 100 mol% of water the catalyst showed significant activity (TOF: 54 h^{-1}).

To classify the potential of our catalytic system we compared Ru(cod)(methylallyl)$_2$/**1** with Ru(cod)(methylallyl)$_2$/PPh_3 and Ru(cod)(methylallyl)$_2$/PCy_3 (Fig. 1). More specifically, we studied the behaviour of Ru(cod)(methylallyl)$_2$/**1** and Ru(cod)(methylallyl)$_2$/PPh_3 by monitoring the conversion at different reaction times. The results showed similar catalytic behaviour at the beginning of the reaction.

Table 2
Influence of metal-ligand-ratio on the reduction of acetophenone (**13**)



Entry	Carbene:metal	Substrate:metal	Base:metal	Time (h)	Yield (%)[c]	TOF (h^{-1})[d]
1[a]	0	100	5	1	41	41
2[a]	1	100	5	1	>99	99
3[a]	2	100	5	1	61	61
4[a]	10	100	5	1	57	57
5[b]	1	5000	100	12	83	346
6[b]	2	5000	100	12	81	338
7[b]	10	5000	100	12	67	279

[a] *Reaction conditions*: *in situ* catalyst: 3.8×10^{-6} mol Ru(cod)(methylallyl)$_2$, 3.8×10^{-6} mol imidazolium salt **1** and 1.9×10^{-5} mol Na–2-OPr in 2.0 mL 2-propanol for 16 h at 65 °C, addition of 3.8×10^{-4} mol acetophenone (**13**), reaction temperature 100 °C.
[b] *Reaction conditions*: *in situ* catalyst: 9.7×10^{-7} mol Ru(cod)(methylallyl)$_2$, 9.7×10^{-7} mol imidazolium salt **1** and 9.7×10^{-5} mol Na–2-OPr in 5.0 mL 2-propanol for 16 h at 65 °C, addition of 4.85×10^{-3} mol acetophenone (**13**), reaction temperature 100 °C.
[c] Conversion is determined by GC analysis (50 m Lipodex E, 95–200 °C) with diglyme as internal standard.
[d] Turnover frequency = mol product/(mol catalyst × time), determined after 12 h.

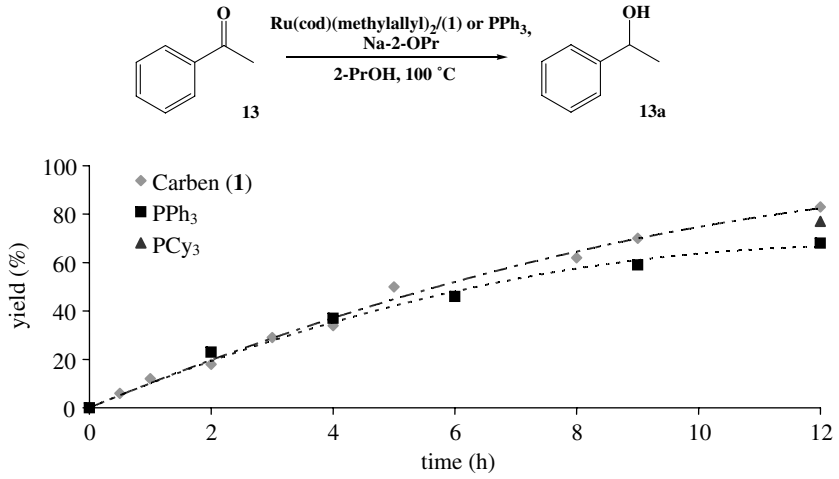


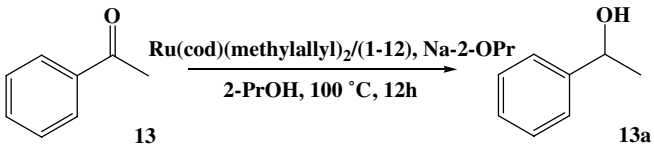
Fig. 1. Comparative study using imidazolium salt **1** and PPh_3 as ligands. *Note*: *Reaction conditions*: *in situ* catalyst: 9.7×10^{-7} mol Ru(cod)(methylallyl)$_2$, 9.7×10^{-7} mol imidazolium salt **1** or PPh_3 and 9.7×10^{-5} mol Na-2-OPr in 5.0 mL 2-propanol for 16 h at 65 °C, addition of 4.85×10^{-3} mol acetophenone (**13**), reaction at 100 °C. Conversion is determined by GC analysis (50 m Lipodex E, 95–200 °C) with diglyme as internal standard.

However, during the reaction a higher deactivation rate of the PPh_3-system is detected, which resulted in a lower yield of 1-phenylethanol after 12 h (68% vs 83%). The Ru(cod)(methylallyl)$_2$/PCy_3 yielded comparable amounts of 1-phenylethanol to Ru(cod)(methylallyl)$_2$/**1**.

As shown in Table 3 we examined 12 examples out of the growing number of carbene precursors (**1**–**12**) under the previously optimized conditions for the transfer hydrogenation of acetophenone (**13**). In order to estimate differences between the various carbene precursors we applied low catalyst loadings (0.02 mol%) at 100 °C. After 12 h average turnover frequencies up to 346 h^{-1} are achieved for the preparation of 1-phenylethanol applying ligand **1**. Summarizing the activities of 4,5-dihydroimidazolium salts, no pronounced influence is observed by variation of substitutents at the nitrogen atoms (2,6-di-*iso*-propylphenyl or mesitylene groups) or by changing the anion of the imidazolium salt (Table 3, entries 2–4). On the other hand by introduction of methyl groups in the 4,5-position of the imidazolium unit a depletion of activity is monitored (Table 3, entries 5 and 6).

In general, application of *N*-alkyl carbenes led to a lower activity compared to *N*-aryl carbenes (Scheme 1, **8**–**12**). In the presence of 1-ethyl-3-methylimidazolium bromide ([EMIM]Br, **11**) and 1-butyl-3-methylimidazolium bromide ([BMIM]Br, **12**), which are usually used as ionic liquids [21], the recorded yields were lower (Table 3, entries 11 and 12).

Table 3
Variation of imidazolium salts in the transfer hydrogenation of acetophenone (**13**)[a]



13 **13a**

Entry	Imidazolium salt	Yield (%)[b]	TOF (h^{-1})[c]	TON[d]
1	1	83	346	4150
2	2	75	313	3750
3	3	68	283	3400
4	4	73	304	3650
5	5	53	221	2650
6	6	61	254	3050
7	7	62	258	3100
8	8	67	279	3350
9	9	77	320	3850
10	10	69	288	3450
11	11	54	225	2700
12	12	38	158	1900

[a] *Reaction conditions*: *in situ* catalyst: 9.7×10^{-7} mol Ru(cod)(methylallyl)$_2$, 9.7×10^{-7} mol imidazolium salt and 9.7×10^{-5} mol Na-2-OPr in 5.0 mL 2-propanol for 16 h at 65 °C, addition of 4.85×10^{-3} mol acetophenone (**13**), reaction for 12 h at 100 °C.

[b] Conversion is determined by GC analysis (50 m Lipodex E, 95–200 °C) with diglyme as internal standard.

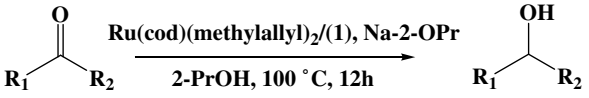
[c] Turnover frequency = mol product/(mol catalyst × time), determined after 12 h.

[d] Turnover number = mol product/mol catalyst, determined after 12 h.

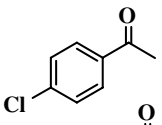
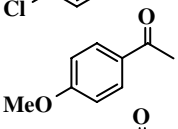
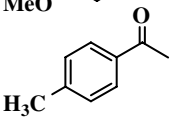
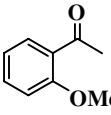
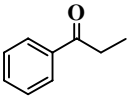
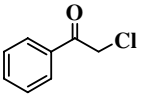
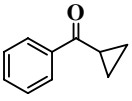
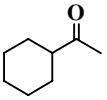
In order to demonstrate the usefulness of the catalysts in a more general manner we employed the catalyst system Ru(cod)(methylallyl)$_2$/**1** in the transfer hydrogenation of nine aromatic and aliphatic ketones (Table 4).

In general, all substrates were hydrogenated with excellent chemoselectivity (>99%). Best activity (TOF up to 338 h^{-1}) is achieved with dialkyl ketones (Table 4, entries

Table 4
Scope and limitations of Ru(cod)(methylallyl)$_2$/**1**-system-catalyzed ketone reduction[a]



14-22 **14a-22a**

Entry	Compound	Ketone	Conversion (%)[b]	TOF (h^{-1})[c]
1	**14**		68 [96]	285
2	**15**		41	171
3	**16**		62 [92]	258
4	**17**		68 [97]	283
5	**18**		67 [93]	281
6	**19**		2	6
7	**20**		40	166
8	**21**		77	321
9	**22**		81	338

[a] *Reaction conditions*: *in situ* catalyst: 9.7×10^{-7} mol Ru(cod)(methylallyl)$_2$, 9.7×10^{-7} mol imidazolium salt **1** and 9.7×10^{-5} mol Na-2-OPr in 5.0 mL 2-propanol for 16 h at 65 °C, addition of 4.85×10^{-3} mol ketone, reaction for 12 h at 100 °C.

[b] Conversion is determined by GC analysis (**14** (25 m Lipodex E, 100 °C), **15** (50 m Lipodex E, 90–105 °C), **16** (25 m Lipodex E, 80–180 °C), **17** (30 m HP Agilent Technologies 50–300 °C), **18** (25 m Lipodex E, 90–180 °C), **19** (50 m Lipodex E, 90–180 °C), **20**–**22** (30 m HP Agilent Technologies 50–300 °C)) with diglyme as internal standard. In brackets the conversion after 24 h is given.

[c] Turnover frequency = mol product/(mol catalyst × time), determined after 12 h.

8 and 9). In comparison, *para*-substituted acetophenones containing an electron-withdrawing group (Table 4, entry 1) showed better conversion than *para*-substituted substrates with an electron-donating group (Table 4, entry 2). Noteworthy, by changing the electron-donating group from *para*- to *ortho*-position a significant increase of the yield is detected (Table 4, entries 2 and 4). We assume for **17** a possible second coordination site at the metal center. No major change in activity is observed for substitution adjacent to the carbonyl group by an ethyl group, whereas introduction of a chloromethyl deactivated the catalyst (Table 4, entries 5 and 6). Moderate activity is monitored when increasing the bulkiness next to the active center by a cyclopropyl group (Table 4, entry 7).

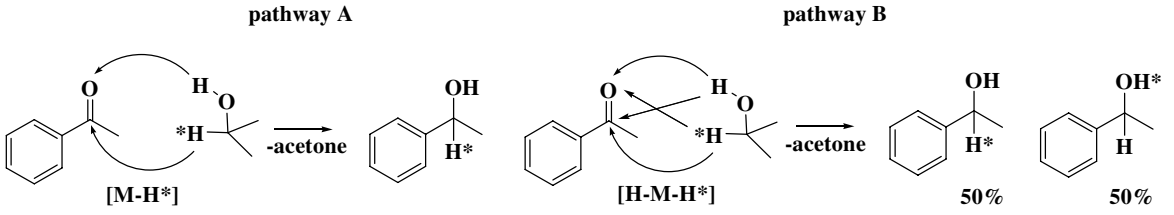
Finally, we were interested in mechanistic aspects. In general, for transition metal catalyzed transfer hydrogenation two mechanisms are accepted, designated as direct hydrogen transfer, via formation of a six-membered cyclic transition state composed of donor, metal and acceptor, and the hydridic route which shows two possible pathways, the monohydride or dihydride mechanism. In more detail, formation of a monohydride-metal-complex promoted an exclusive hydride transfer from carbon (donor) to carbonyl carbon (acceptor) (Scheme 2, pathway A), whereas a hydride transfer from carbon (donor) to carbonyl carbon (acceptor) as well as to the carbonyl oxygen (acceptor) was proposed for a dihydride-metal-complex formation (Scheme 2, pathway B). Indications for both pathways were published by Bäckvall et al. and other groups, when following the hydride transfer catalyzed by various metal complexes [22].

Mechanistic studies have been mostly published for catalysts containing phosphines, amines or cyclopentadienyls as ligands [22a]. For transition metal complexes containing carbene ligands Faller and Crabtree described investigations on an iridium dicarbene system [16c]. They assumed a monohydride mechanism, because the hydride is mainly transferred in the 1-position of acetophenone. So far there is no mechanistic investigation known in transfer hydrogenations applying Ru carbene catalysts.

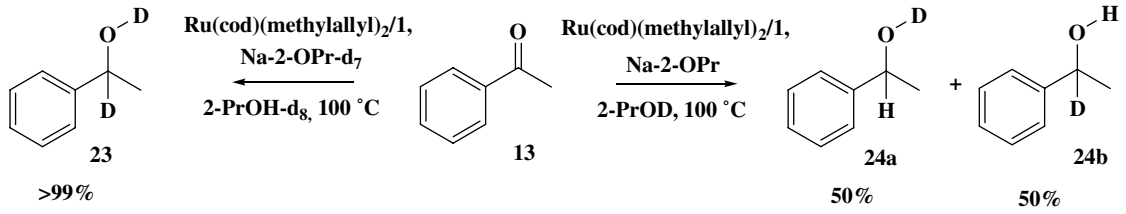
Reaction of ketone **20** (''radical clock''-substrate) with 2-propanol in the presence of 1 mol% Ru(cod)(methylallyl)$_2$/**1** gave only the corresponding cyclopropyl phenyl alcohol (>99% by ^{1}H NMR). Apparently, there is no radical induced reduction [23]. Owing to this a radical reduction mechanism promoted by sodium alkoxides can be also excluded, whereby the transition metal plays only a marginal role [24]. This assumption is also confirmed by performing the reduction of acetophenone (**13**) in the presence of base and in the absence of ruthenium catalyst. Here, no reduction product was detected.

Next, we followed the transfer of hydrogen from the donor molecule into the product by applying a deuterated donor [25]. The catalytic precursor is generated by stirring a solution of 2-propanol-d$_8$, Ru(cod)(methylallyl)$_2$ and imidazolium salt **1** in the presence of sodium 2-propanolate-d_7 for 16 h at 65 °C. Then, acetophenone (**13**) was added and the solution was stirred for 30 min at 100 °C. As main product (>99%) **23** was observed by ^{1}H NMR (Scheme 3) [26]. The result showed an exclusive transfer of the deuterium into the carbonyl group, so that no C–H activation on the substrate occurred under the described conditions. Furthermore, this result rules out enol formation in the catalytic cycle [27].

To clarify the transfer of hydrogen from the hydrogen donor into the substrate the reaction was run with 2-propanol-d_1 (hydroxy-group deuterated) as solvent/donor and sodium 2-propylate as base. In the transfer hydrogenation of acetophenone (**13**) we obtained a mixture of two different deuterated 1-phenylethanols (Scheme 2, **24a** and **24b**). Here, a scrambling of the transferred proton and deuteride is found (**24a** and **24b** = 1:1). In conclusion the non-specific



Scheme 2. Comparison of monohydride and dihydride mechanism for transfer hydrogenations.



Scheme 3. Deuterium incorporation into acetophenone catalyzed by Ru(cod)(methylallyl)$_2$/**1**-system in the presence of base.

migration is in agreement with the dihydride mechanism, implying a formation of metal dihydride species in the catalytic cycle [2d].

3. Summary

We demonstrated the successful application of *in situ* prepared ruthenium catalysts containing carbene ligands in the transfer hydrogenation of various ketones. In the reduction of acetophenone (**13**) turnover frequencies up to 346 h^{-1} were found for a catalyst system containing Ru(cod)(methylallyl)$_2$/1,3-bis(2,6-di-*i*-propylphenyl)-imidazolium chloride (**1**). Mechanistic experiments indicated the transfer of hydrogen from the donor molecule into the substrate via a dihydride mechanism.

4. Experimental section

4.1. General

All manipulations were performed under argon atmosphere using standard Schlenk techniques. Unless specified, all chemicals are commercially available and used as received. Sodium 2-propylate was prepared by reacting sodium with 2-propanol under an argon atmosphere. 2-Propanol was used without further purification (purchased from Fluka, dried over molecular sieves). Imidazolium salts **1**, **2**, **5**, **6**, **8** and **9** were synthesized according to the published protocols [4,28]. Imidazolium salts **11** and **12** were a gift by Solvent Innovation. Imidazolium salts **3**, **4**, **7** and **10** are commercially available by Strem. All ketones were dried over CaH_2, distilled in vacuum and stored under argon, except ketones **17** and **19**, which were cycled with vacuum-argon and stored under argon.

4.2. General procedure for catalytic transfer hydrogenation of ketones

In a 10 mL Schlenk tube, the *in situ* catalyst (9.7×10^{-7} mol) was prepared by stirring a solution of Ru(cod)(methylallyl)$_2$ (9.7×10^{-7} mol), imidazolium salt (9.7×10^{-7} mol) and sodium 2-propylate (4.85×10^{-6} mol) in 1.0 mL 2-propanol for 16 h at 65 °C. After addition of the corresponding ketone (4.85×10^{-3} mol) and the internal standard diglyme in 4.0 mL 2-propanol the Schlenk tube was sealed and the reaction mixture was heated to 100 °C. After 12 h the conversion was measured by GC without further purification. In the case of ^{1}H NMR determination of the yield, the solvent was removed in vacuum and the residue was dissolved in $CDCl_3$ and submitted to ^{1}H NMR.

4.3. Procedure for transfer hydrogenation of acetophenone with 2-propanol-d_8 as hydride source

In a 10 mL Schlenk tube, Ru(cod)(methylallyl)$_2$ (3.8×10^{-6} mol), imidazolium salt **1** (3.8×10^{-6} mol) and sodium 2-propylate-d_7 (1.9×10^{-5} mol, prepared by reacting sodium with 2-propanol-d_8) was solved in 1.0 mL 2-propanol-d_8 and stirred for 16 h at 65 °C. After addition of the acetophenone (**13**) (3.8×10^{-4} mol) in 2.0 mL 2-propanol-d_8 the reaction mixture was heated to 100 °C for 30 min. The solution was cooled to r.t. and filtrated over a plug of silica. The conversion was determined by ^{1}H NMR.

4.4. Procedure for transfer hydrogenation of acetophenone with 2-propanol-d_1 as hydride source

In a 10 mL Schlenk tube, Ru(cod)(methylallyl)$_2$ (3.8×10^{-6} mol), imidazolium salt **1** (3.8×10^{-6} mol) and sodium 2-propylate (1.9×10^{-5} mol, prepared by reacting sodium with 2-propanol) was solved in 1.0 mL 2-propanol-d_1 (deuterium fixed as hydroxyl proton) and stirred for 16 h at 65 °C. The reaction mixture was heated to 100 °C for 10 min after addition of the acetophenone (**13**) (3.8×10^{-4} mol) in 2.0 mL 2-propanol-d_1. (To avoid side effects reaction was not run to full conversion.) The solution was cooled to r.t. and filtrated over a plug of silica. The solvent was removed in vacuum and the residue was solved in $CDCl_3$. The conversion was determined by ^{1}H NMR.

4.5. Product characterization

The obtained alcohols are known compounds. They were characterized by comparison with authentic samples and mass spectroscopy (Agilent Technologies 6890N, MSD 5973) or ^{1}H NMR (Bruker ARX-400). Product **13a:** *m*/*z* (%) = 122 (M^+, 21); 107 (72); 79 (100); 51 (34); 43 (36); 39 (13); 32 (15). Product **14a**: *m*/*z* (%) = 156 (M^+, 26); 141 (100); 121 (14); 113 (33); 103 (9); 77 (85); 51 (12); 43 (22). Product **15a**: *m*/*z* (%) = 152 (M^+, 24); 137 (100); 134 (32); 119 (20); 109 (48); 94 (38); 91 (34); 77 (46); 65 (31); 51 (16); 43 (37); 39 (21). Product **16a**: *m*/*z* (%) = 136 (M^+, 32); 121 (100); 117 (14); 91 (94); 77 (53); 65 (29); 51 (16); 43 (57); 39 (23). Product **17a**: *m*/*z* (%) = 152 (M^+, 31); 137 (100); 134 (20); 119 (10); 109 (46); 94 (29); 91 (16); 77 (28); 65 (12); 43 (13). Product **18a**: *m*/*z* (%) = 152 (M^+, 11); 107 (100); 79 (79); 51 (13). Product **19a**: *m*/*z* (%) = 156 (M^+, 3); 107 (100); 91 (7); 79 (67); 77 (50); 51 (19). Product **20a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.34 (1H, m); 0.44 (1H, m); 0.51 (1H, m); 0.58 (1H, m); 1.00 (1H, m); 2.31 (1H, s); 3.98 (1H, d, J = 8.16 Hz); 7.24 (3H, m); 7.99 (1H, d, J = 7.52 Hz). Product **21a**: *m*/*z* (%) = 128 (M^+, 17); 110 (34); 95 (18); 81 (100); 67 (71); 55 (78); 41 (46). Product **22a**: *m*/*z* (%) = 102 (M^+, 3); 87 (26); 57 (100); 45 (83); 41 (53).

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