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Transfer hydrogenation of unfunctionalised alkenes using *N*-heterocyclic carbene ruthenium catalyst precursors

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Transfer hydrogenation of unfunctionalised and aliphatic alkenes in *i*PrOH/KOH is efficiently catalysed by an olefin-tethered *N*-heterocyclic carbene ruthenium complex, which also catalyses double bond migration as a competitive and considerably faster process.

Homogeneous hydrogenation of olefins is classically performed by direct hydrogenation using molecular H_2.[1] In contrast, transfer hydrogenation of olefins from an immobilised hydrogen source[2] is rare,[3,4] and involves in most cases a heterogeneous catalytic phase.[4] The low abundance of transfer hydrogenation for olefin reduction appears rather surprising when considering that the catalytically active species for direct hydrogenation and transfer hydrogenation are closely related. Both methods require a metal-dihydride species, or a monohydride complex when a ligand or extraneous auxiliary is assisting the H_2 or hydrogen-donor activation.[1,2] A distinct number of complexes are indeed known to catalyse hydrogenations both *via* transfer or direct hydrogenation.[5] However, these systems are often limited to polarised substrates,[6] or display only low activity towards olefins.[7]

We have recently observed that ruthenium complexes comprising a chelating *N*-heterocyclic carbene (NHC) ligand are catalyst precursors both for the direct hydrogenation of olefins[8] as well as for the transfer hydrogenation of ketones and polarised C=C bonds,[9] indicating that the catalytically active species may be accessible either *via* H_2 activation or *via* *i*PrOH activation, and that this species is able to hydrogenate both styrene (established for direct hydrogenation) or ketones (*via* hydrogen transfer). Here we report on a combination of these concepts and demonstrate the effective transfer hydrogenation of unactivated and aliphatic olefins.

Complexes **1–4**[8] (Fig. 1) were evaluated as catalyst precursor (1 mol% loading) in the transfer hydrogenation of 1-dodecene as a model substrate of an unfunctionalised and unactivated alkene, using classical[2] hydrogen transfer conditions (KOH as base, *i*PrOH as solvent and hydrogen source, Table 1).† The four catalyst precursors displayed strongly diverging behaviour. Complex **2** was completely inactive. When using complex **3**, all starting material was consumed within 5 h and the solution was comprised predominantly of isomeric dodecene mixtures (76%) and dodecane (24%). Prolonged heating gave only a slight increase of hydrogenated product (32% dodecane after 24 h, Table 1). The activity of complex **4** was similar to that of **3** after 5 h (37% hydrogenated product, 63% dodecenes), yet hydrogenation continued and reached 79% after 24 h. Significant higher transfer activity was observed for the olefin-functionalised NHC complex **1**, which induced consumption of all starting material within 30 min and complete hydrogenation within 24 h.

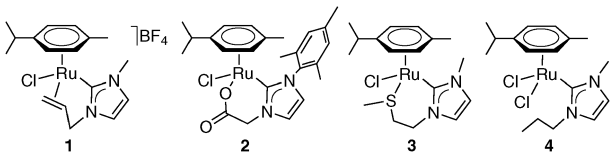

Fig. 1 Catalyst precursors for the transfer hydrogenation of olefins.

These initial studies suggested that coordinative lability of one ligand (site) is important to induce catalytic activity. This hypothesis is supported by the results from catalytic runs performed with complex **4** after activation with one mol equiv. $AgBF_4$ in order to abstract one chloride ligand from the precursor.[9,10]‡ Transfer hydrogenation under these conditions was significantly accelerated, reaching 81% dodecane formation after 5 h (*cf.* 61% with **1**). The increased catalytic activity is also reflected by the higher turnover frequency at 50% conversion, TOF_{50} = 12 h^{-1} for **1** and 19 h^{-1} for activated **4**. However, the catalyst robustness deteriorated and the hydrogenation ceased after *ca.* 90% conversion, while complex **1** showed prolonged activity and reached full conversion.

Table 1 Catalytic transfer hydrogenation of 1-dodecene[a]

	% Yield (dodecane/dodecenes)[b]							
Complex	0.5 h		2 h		5 h		24 h	
1	100	(9/91)	100	(25/75)	100	(61/39)	100	(100/0)
2	0	(0/0)	0	(0/0)	0	(0/0)	0	(0/0)
3	50	(11/39)	87	(23/64)	100	(24/76)	100	(32/68)
4	67	(7/60)	95	(16/79)	100	(37/63)	100	(79/21)
4 + BF_4	95	(20/75)	100	(42/58)	100	(81/19)	100	(89/11)

[a] General conditions: 1-dodecene (2.0 mmol), KOH (0.2 mmol), complex (20 μmol; S/B/C 100 : 10 : 1), and 3,5-dimethylanisole (80 μL, internal standard) in *i*PrOH (10 mL), 80 °C (reflux). [b] conversion determined by ^{1}H NMR spectroscopy and GC-MS, dodecenes are mixtures of isomers.

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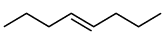
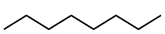
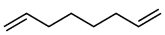
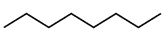
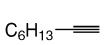
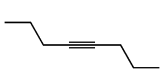
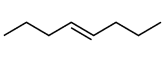
Catalyst robustness may be enhanced by the presence of the hemilabile olefin group, though it remains limited. Upon reducing the loading of complex **1** from 1 mol% to 0.1 mol%, activity is preserved for the first 5 h (51% hydrogenated product formed), though drops substantially after that time and resulted in a mere 59% conversion to dodecane after 24 h, corresponding to a total turnover number of 590. Efficient hydrogenation is evidently compromised by a latent catalyst instability, presumably associated with slow hydrogenation of the olefin wingtip group of the NHC ligand.

The scope and limitation of this transfer hydrogenation was examined by using complex **1** as catalyst precursor for the hydrogenation of different olefin substrates (Table 2). Styrene was converted to ethylbenzene in moderate 30% after 24 h. Di-arylated olefins were less reactive and both *cis*- and *trans*-stilbene were hydrogenatated to diphenylethane only in trace amounts (entries 3, 4). The main process with *cis*-stilbene was the expected isomerisation to the thermodynamically more stable *trans*-isomer (42% after 0.5 h).[11] Allylbenzene, and in particular *β*-methylstyrene were significantly faster converted, providing 48% and 92% propylbenzene, respectively (entries 5, 6).§ Cyclooctene (coe) was used as a substrate to probe the preference for terminal *vs.* internal olefins (entry 7). Hydrogenation rates to cyclooctane were comparable to those of dodecene. A competition experiment using 50 mol equiv. dodecene and 50 mol equiv. coe confirmed the absence of any discrimination of these two substrates, and both cyclooctane and dodecane were produced at essentially identical rates as in independent runs using pure substrates. Apparently, ruthenium coordination by *cis*-olefins (*cf.* coe) is not significantly different from coordination by dodecene,[12] which may occur through a *cis*-, *trans*-, or terminal olefin due to the high isomerisation activity of the ruthenium catalyst. In line, internal linear olefins were equally susceptible to transfer hydrogenation (entry 8). Dienes were converted less cleanly. For example, hydrogenation of *α*,*ω*-octadiene produced 54% monohydrogenated octene and 15% fully hydrogenated octane (84 turnovers) after 24 h (entry 9), isomerisation was again considerably faster (31% conversion after 10 min).

Table 2 Transfer hydrogenation of different olefins using complex **1**[a]

Entry	Substrate	Product	Conversion (24 h)
1			100%
2			30%
3			7%
4			7%
5			48%
6			92%
7			100%
8			84%
9			15%[b]
10			17%
11			9%
12			21%[c]

[a] General conditions identical to Table 1. [b] 54% monohydrogenated octene formed as mixture of isomers. [c] and other isomers of octene.

Limited reactivity was observed in the transfer hydrogenation of alkynes. Phenylacetylene, and terminal or internal aliphatic alkynes were converted only in minor quantities (entries 10–12). Interestingly, in all cases semi-hydrogenation occurred, perhaps due to tighter bonding of alkynes as opposed to alkenes, and the corresponding olefins were the only observed products.[13]

The catalytic species remains active upon repetitive addition of 1-dodecene. Addition of new substrate (100 mol equiv.) after 2, 4, and 6 h indicated full consumption of the substrate within the subsequent 2 h (Fig. 2). However, the relative ratio of isomerised *vs.* hydrogenated product gradually increased from 3 : 2 after converting the first batch to 3 : 1 after the third batch, and 18 h reaction time were required to achieve the initial 3 : 2 ratio after adding the forth batch of substrate (172 TONs). The continuous decrease of transfer hydrogenation activity (total TONs are 41, 74, and 78 after 2, 4, and 6 h, respectively) indicates a limited stability of the catalytically active species, thus corroborating the results obtained from catalytic runs with lowered catalyst loading (*vide supra*).

Further mechanistic insights were obtained from experiments in perdeuterated isopropanol (*i*PrOD–D_8) as solvent. The formed dodecane contained deuterium in both the terminal and internal positions (2 : 7 integral ratio in the ^{2}H NMR spectrum). This ratio suggests rapid isomerisation, presumably *via* a π-allylic mechanism rather than a 2,1-alkene insertion/*β*-H elimination process, in which a ruthenium-bound hydride rapidly undergoes H/D exchange with *i*PrOD–D_8.[14] Complementary analyses by HRMS revealed a multitude of dodecane isotopes, ranging from monodeuterated dodecane to dodecane–D_{19}.

Catalytic runs in the presence of mercury provided ambivalent results.[15] Addition of a large excess (350 mol equiv.) of Hg^0 to the catalytic mixture after 10 min reaction time, when the reaction mixture comprised 74% 1-dodecene, 23% isomerised dodecenes, and 3% hydrogenated dodecane,[16] did not stop the consumption of the starting material, yet decelerated transfer hydrogenation substantially. After 5 h, only 23% dodecane was formed and 34% after 24 h (*cf.* 61% and 100%, respectively, in the absence of mercury). Hydrogen transfer was thus ongoing, albeit much slower. Isomerisation was also affected, yet not inhibited, by the presence of mercury, and almost 5 h were required for the complete isomerisation of 1-dodecene to internal olefins. While mass transport limitations may be effective, we cannot rule out the presence of different mechanisms for the olefin transfer hydrogenation. For example,

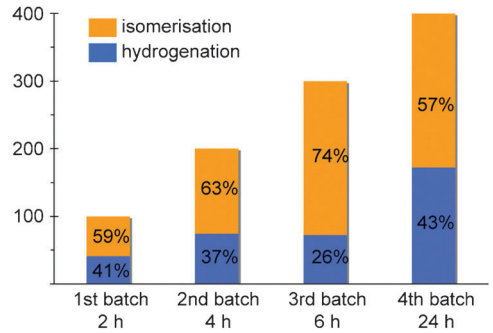


Fig. 2 Composition of reaction mixtures of multi-batch experiments with complex **1** before introducing additional batches of substrate after 2, 4, and 6 h (4 batches added in total) revealing full conversion of each batch, yet gradual decrease of hydrogenation activity.

a parallel heterogeneous pathway[17] may be suppressed by mercury, thus rationalising the slower product formation. Previous experiments under identical reaction conditions using a ketone as hydrogen acceptor did reveal non-sigmoidal kinetics,[9] which is in agreement with molecular homogeneous catalysis.[15] However, complex **1** was also shown to decompose to a catalytically competent species under harsher conditions (60 bar H_2).[8] Catalytic runs with substoichiometric quantities of complex **1** revealed partial hydrogenation of the olefin wingtip group[18] along with significant decomposition products, though it is unclear whether wingtip hydrogenation and complex degradation occurred before or after substrate hydrogenation.

In conclusion, transfer hydrogenation of unfunctionalised alkenes was accomplished using NHC ruthenium complexes. The substitution pattern at the NHC ligand plays a critical role, and highest activity as well as sufficient robustness was achieved with a potentially hemilabile olefin as chelating wingtip group. Olefin isomerisation is a significantly faster process and presumably facilitates the hydrogenation of internal alkenes *via* double bond migration to terminal positions. A limitation of the NHC ruthenium complexes constitutes the stability of the catalytically active species, which prevents conversions at low catalyst loading and restricts catalytic activity upon repetitive substrate addition. Appropriate engineering of the NHC ligand may allow these drawbacks to be eliminated.

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Notes and references

† Representative catalytic procedure: A 25 mL oven-dried Schlenk-tube was charged under N_2 with anhydrous *i*PrOH (10 mL). The solvent was degassed *via* 3 freeze-pump-thaw cycles and the ruthenium complex (20 μmol) was added and dissolved by sonication (10 min, 40 °C). Then KOH (0.1 mL, 2M in H_2O, 0.2 mmol) was introduced and the mixture pre-heated to 90 °C for 10 min before the substrate (2.0 mmol) and 3,5-dimethylanisole (80 μL, 0.6 mmol as internal standard) were added. Aliquots (0.2 mL) were taken at fixed times, quenched with pentane (1 mL), and filtered through a short pad of silica. The silica was washed with Et_2O (2 mL) and the combined organic filtrates were analysed by GC-MS and, after careful evaporation, by ^{1}H NMR spectroscopy.

‡ A procedure was used as described above, except for adding $AgBF_4$ (3.9 mg, 20 μmol) to the light-protected solution of complex **4** and stirring for 2 min before adding the base and the substrate.

§ Since for allylbenzene, isomerisation was again a competing and much faster process than hydrogenation (after 10 min, approximately 50% conversion to *β*-methylstyrene and 6% hydrogenated product was observed), we would have expected similar rates for the transfer hydrogenation of allylbenzene and *β*-methylstyrene, however, the former was reproducibly converted at slower rates.

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