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

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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 iPrOH/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 H₂. In contrast, transfer hydrogenation of olefins from an immobilised hydrogen source is rare, and involves in most cases a heterogeneous catalytic phase. 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 H₂ or hydrogen-donor activation. A distinct number of complexes are indeed known to catalyse hydrogenations both via transfer or direct hydrogenation. However, these systems are often limited to polarised substrates, or display only low activity towards olefins.

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 as well as for the transfer hydrogenation of ketones and polarised C=C bonds, indicating that the catalytically active species may be accessible either via H₂ activation or via iPrOH 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 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 hydrogen transfer conditions (KOH as base, iPrOH 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.

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. AgBF₄ in order to abstract one chloride ligand from the precursor. 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, TOFₜ₀ = 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. 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%
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.

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 (vide supra) after 24 h (entry 9), isomerisation was again considerably faster (31% conversion after 10 min).

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.

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. 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 perdeuterio isopropanol (iPrOD–D₄) as solvent. The formed dodecane contained deuterium in both the terminal and internal positions (2:7 integral ratio in the ²H 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 iPrOD–D₄. Complementary analyses by HRMS revealed a multitude of dodecane isotopes, ranging from monodeuterated dodecane to dodecane–D₉.

Catalytic runs in the presence of mercury provided ambivalent results. Addition of a large excess (350 mol equiv.) of Hg to the catalytic mixture after 10 min reaction time, when the reaction mixture comprised 74% 1-dodecene, 23% isomerised dodecenes, and 3% hydrogenated dodecane,

Table 2 Transfer hydrogenation of different olefins using complex 1 +

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate</th>
<th>product</th>
<th>conversion (24 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₆H₆H₆</td>
<td>C₆H₆H₆</td>
<td>100%</td>
</tr>
<tr>
<td>2</td>
<td>Ph</td>
<td>Ph</td>
<td>30%</td>
</tr>
<tr>
<td>3</td>
<td>Ph</td>
<td>Ph</td>
<td>7%</td>
</tr>
<tr>
<td>4</td>
<td>Ph</td>
<td>Ph</td>
<td>7%</td>
</tr>
<tr>
<td>5</td>
<td>Ph</td>
<td>Ph</td>
<td>48%</td>
</tr>
<tr>
<td>6</td>
<td>Ph</td>
<td>Ph</td>
<td>92%</td>
</tr>
<tr>
<td>7</td>
<td>Ph</td>
<td>Ph</td>
<td>100%</td>
</tr>
<tr>
<td>8</td>
<td>Ph</td>
<td>Ph</td>
<td>84%</td>
</tr>
<tr>
<td>9</td>
<td>Ph</td>
<td>Ph</td>
<td>15% b</td>
</tr>
<tr>
<td>10</td>
<td>Ph</td>
<td>Ph</td>
<td>17%</td>
</tr>
<tr>
<td>11</td>
<td>C₆H₆</td>
<td>C₆H₆</td>
<td>9%</td>
</tr>
<tr>
<td>12</td>
<td>C₆H₆</td>
<td>C₆H₆</td>
<td>21% c</td>
</tr>
</tbody>
</table>

* General conditions identical to Table 1.  * 54% monohydrogenated octene formed as mixture of isomers.  + other isomers of octene.

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% 24 h. Di-arylated olefins were less reactive and both cis- and transstilbene were hydrogenated 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). 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 dodecane. 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 cyclooctene 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, which may occur through a cis-, trans- or terminal olefin due to the high isomerisation activity of the ruthenium catalyst. In line,
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, a parallel heterogeneous
pathway\(^9\) 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,\(^{2}\) which is in
agreement with molecular homogeneous catalysis.\(^3\) However,
complex I was also shown to decompose to a catalytically
competent species under harsher conditions (60 bar H\(_2\)).\(^9\)
Catalytic runs with substoichiometric quantities of complex I
revealed partial hydrogenation of the olefin wingtip group;
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

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† Representative catalytic procedure: A 25 mL oven-dried Schlenk-tube
was charged under N\(_2\) with anhydrous iPrOH (10 mL). The solvent
was degassed via 3 freeze-pump-thaw cycles and the ruthenium complex
(20 \(\mu\)mol) was added and dissolved by sonication (10 min, 40 °C). Then KOH
(0.1 mL, 2M in H\(_2\)O, 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 \(\mu\)L, 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\(_2\)O (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 \(\mu\)mol) 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 \(\beta\)-methylstyrene and 6% hydrogenated product was observed), we
would have expected similar rates for the transfer hydrogenation of
allylbenzene and \(\beta\)-methylstyrene, however, the former
was reproducibly converted at slower rates.

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