Rapid Communication

Ligands and Ru catalysts, Ru DAB, Salen and DMSO complexes catalyzed selective transfer hydrogenation of ketones and aldehydes

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Salen, DAB and DMSO Ru complexes are excellent catalysts for the transfer hydrogenation of ketones and aldehydes using i-C₃H₇OH as the transfer hydrogenating agent. The reduction of ketones and aldehydes is selective in the presence of olefins with Ru DMSO complex. The transfer hydrogenations can be carried out at room temperature with the Ru DMSO catalysts in high yields.

Catalytic transfer hydrogenation has gained tremendous importance in the laboratory for the reduction of various functional groups. HCOONH₄ and isopropyl alcohol are two of the most common reducing agents. The dramatic accelerating effect of NaOH/KOH as co-catalyst for the transfer hydrogenation of ketones and aldehydes using Ru catalysts was demonstrated by Backvall et al. Rh, Ir and Ru complexes are mostly used for such reductions. Asymmetric transfer hydrogenations have been carried out using chiral ligands. We and others have demonstrated the use of Ni salts and complexes as catalyst alternatives for such transfer hydrogenations.

Salen and DMSO complexes of Ru, Rh, Pd have been mostly used for the hydrogenation of olefins. Co salen supported on zeolite and aminosulfoxide Ir complexes have been used for the reduction of ketones. Phosphines, PNNP, ethanol amines, diamines, have been used as ligands in the Ru catalyzed transfer hydrogenations and the corresponding chiral ligands give very high asymmetric inductions. A tridentate chiral P, N, O Schiff base ligand has been used in situ with Ru(DMSO)₄Cl₂ for the asymmetric transfer hydrogenation of acetophenone in 81% ee. In our search for efficient transfer hydrogenation catalysts, we also investigated the effect of novel ligands in these reactions.

Salen, DAB and DMSO are readily available non-phosphorous ligands and excellent alternatives for the currently used phosphines, ethanol amines, diamines and other ligands, for routine transfer hydrogenations not requiring asymmetric induction. These ligands have been mostly used for hydrogenation of olefins, and only in a few cases, supported on zeolites or as chelating ligands for transfer hydrogenation of ketones. A variety of these ligands can be readily synthesized from commercially available precursors with substituents to influence the catalytic properties and asymmetric induction.

The transfer hydrogenation of acetophenone, benzalacetone, cinnamaldehyde and citral in the presence of these catalysts with KOH as co-catalyst in i-C₃H₇OH, gave high yields of the corresponding alcohol (Scheme I). RuCl₂(DAB)₂ (Cat-1), salen (Cat-2), DMSO (Cat-3), DMSO-P(C₆H₅)₃ (Cat-4) complexes were prepared by known procedures (Figure 1).

Transfer hydrogenation with salen, DAB Ru complex of acetophenone, anisaldehyde gave 77-93% yield in 8-12 hr. Reduction with the DAB Ru (Cat-1) took longer time. Benzalacetone, cinnamaldehyde,

\[
\text{Cat-1} : \text{Ru(DAB)₂Cl₂} \\
\text{Cat-2} : \text{Ru(salen)P(C₆H₅)₃Cl} \\
\text{Cat-3} : \text{Ru(dmsos)₄Cl₂} \\
\text{Cat-4} : \text{Ru(dmsos)₃P(C₆H₅)₃Cl₂}
\]

Scheme I Transfer hydrogenation of aldehydes and ketones

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**Figure 1**—Ru catalysts for transfer hydrogenation

<table>
<thead>
<tr>
<th>Sl.</th>
<th>Carbonyl compound (mmole)</th>
<th>Catalyst (mmole)</th>
<th>Time (hr)</th>
<th>Temp</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>C₆H₅COCH₃ (5)</td>
<td>Ru DAB-1 (0.025)</td>
<td>14</td>
<td>reflux</td>
<td>80</td>
</tr>
<tr>
<td>2.</td>
<td>C₆H₅COCH₃ (3)</td>
<td>Ru Salen. P(C₆H₅)₂ (0.04)</td>
<td>10</td>
<td>reflux</td>
<td>82</td>
</tr>
<tr>
<td>3.</td>
<td>C₆H₅COCH₃ (2)</td>
<td>Ru (DMSO)-3 (0.1)</td>
<td>8</td>
<td>reflux</td>
<td>85</td>
</tr>
<tr>
<td>4.</td>
<td>C₆H₅COCH₃ (3)</td>
<td>Ru (DMSO).P(C₆H₅)₂ (0.025)</td>
<td>24</td>
<td>RT</td>
<td>84.7</td>
</tr>
<tr>
<td>5.</td>
<td>4-CH₃O.C₆H₄CHO (5)</td>
<td>Ru DAB-1 (0.025)</td>
<td>10</td>
<td>reflux</td>
<td>86.5</td>
</tr>
<tr>
<td>6.</td>
<td>4-CH₃O.C₆H₄CHO (3)</td>
<td>Ru Salen-2 (0.04)</td>
<td>8</td>
<td>reflux</td>
<td>93</td>
</tr>
<tr>
<td>7.</td>
<td>4-CH₃O.C₆H₄CHO (3)</td>
<td>Ru DMSO)-3 (0.049)</td>
<td>30 (min)</td>
<td>reflux</td>
<td>92.5</td>
</tr>
<tr>
<td>8.</td>
<td>4-CH₃O.C₆H₄CHO (3)</td>
<td>Ru DMSO)-3 (0.04)</td>
<td>24</td>
<td>RT</td>
<td>85</td>
</tr>
<tr>
<td>9.</td>
<td>4-CH₃O.C₆H₄CHO (3)</td>
<td>Ru (DMSO).P(C₆H₅)₂ (0.025)</td>
<td>24</td>
<td>RT</td>
<td>91.8</td>
</tr>
<tr>
<td>10.</td>
<td>4-CH₃O.C₆H₄CHO (3)</td>
<td>Ru (DMSO).P(C₆H₅)₂ (0.025)</td>
<td>25 (min)</td>
<td>reflux</td>
<td>96</td>
</tr>
<tr>
<td>11.</td>
<td>10-C₆H₅CH=CH.CO.CH₃ (3)</td>
<td>Ru (DMSO)-3 (0.049)</td>
<td>17</td>
<td>reflux</td>
<td>90</td>
</tr>
<tr>
<td>12.</td>
<td>10-C₆H₅CH=CH.CO.CH₃ (3)</td>
<td>Ru (DMSO)-3 (0.04)</td>
<td>12</td>
<td>RT</td>
<td>88.3</td>
</tr>
<tr>
<td>13.</td>
<td>10-C₆H₅CH=CH.CO.CH₃ (3)</td>
<td>Ru (DMSO).P(C₆H₅)₂ (0.025)</td>
<td>24</td>
<td>RT</td>
<td>71</td>
</tr>
<tr>
<td>14.</td>
<td>4-C₆H₅CH=CH.CO.CH₃ (3)</td>
<td>Ru (DMSO)-3 (0.04)</td>
<td>3</td>
<td>RT</td>
<td>86.8</td>
</tr>
<tr>
<td>15.</td>
<td>Citral (3)</td>
<td>Ru (DMSO)-3 (0.04)</td>
<td>3</td>
<td>RT</td>
<td>86.8</td>
</tr>
</tbody>
</table>

*a: Reaction conditions- Acetophenone : 3 mmole, Cat-1 [RuCl₂(DAB)₂] 0.025 mmole, KOH : 0.357 mmole, i-C₆H₁₂OH : 15 mL, reflux, 14 hr, 80% yield of α-phenethyl alcohol; All reaction products are known compounds and characterized by ¹H NMR and IR*
anisaldehyde and citral gave high yields with selectivity for the carbonyl group. The reductions of acetophenone, cinnamaldehyde, benzalacetone, anisaldehyde, citral at reflux temperature took 30 min-10 hr compared to 3-24 hr at room temperature.

The Ru (DMSO)$_3$P(C$_6$H$_5$)$_3$ (Cat-4) complex also gave high yields (84-91%) for reduction of acetophenone, benzalacetone and anisaldehyde at room temperature in 12-24 hr. The results are shown in Table I. Ru(DMSO)$_3$Cl$_2$ complex gave the highest yield for the transfer hydrogenation of acetophenone (85% yield in 8 hr) and anisaldehyde (92.5% yield in 25 min) at 110-120 °C. Benzalacetone (96% yield in 25 min) also gave the highest yields in the shortest reaction times with this catalyst.

Sulfoxides, salen and DAB are excellent ligands for Ru catalyzed transfer hydrogenation. Asymmetric induction in transfer hydrogenations with chiral ligands and catalysts would be extremely facile with opportunity for easy variations in functional group substitutions in the ligands to affect both reactivity and selectivity.

**Typical procedure**

Acetophenone (0.240 g, 2 mmole), Ru(DMSO)$_3$Cl$_2$ (Cat-3, 0.048 g, 0.1 mmole), KOH (0.020 g, 0.357 mmole) as co-catalyst, were taken in a flask containing 15 mL i-C$_3$H$_7$OH and refluxed for 8 hr under Ar. Evaporation of solvent on a rotary evaporator, dilution with water, extraction (ethyl acetate- 3 × 25 mL), followed by concentration and purification by column chromatography over silica gel (100-200 mesh) gave 0.208 g (85% yield) of α-phenethyl alcohol.

**References**