Ruthenium(II) Complexes with New Tridentate Ligands containing P, N, O Donor Atoms: Highly Efficient Catalysts for Transfer Hydrogenation of Ketones by Propan-2-ol

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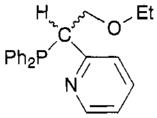
The complexes [$RuCl_2(PPh_3)(L)$] in which L is a tridentate ligand with P, N and O donor atoms are very efficient catalysts for the transfer hydrogenation of cyclic ketones and acetophenone (turnover $\leqslant$ 118 800 h^{-1}) in basic media; when L is optically active, no significant e.e. is observed.

We have recently described the new ligand 1-(diphenylphosphino)-2-ethoxy-1-(2-pyridyl)ethane **1** and shown that it can be either bidentate (P, N) or tridentate (P, N, O) towards various metals.[1] For instance, the reaction of 2 equiv. of **1** with [$RuCl_2(PPh_3)_3$] leads to the formation of [$RuCl_2(\mathbf{1})_2$] in which **1** is (P, N) bound[1] but, more recently[2] we have observed that, when the reaction is conducted with only 1 equiv. of **1**, the complex **2** [$RuCl_2(PPh_3)(\mathbf{1})$] is obtained in good yield. In this compound the ligand **1** is (P, O, N) bound and the ether arm has hemilabile character.[3] This property should induce catalytic activity in the resulting complexes[3] and prompted us to explore the catalytic properties of **2**. We report here the remarkable results obtained for the **2**-catalysed transfer hydrogenation of ketones by propan-2-ol, and the extension to other complexes [$RuCl_2(PPh_3)(L)$] in which L is optically active and (P, O, N) tridentate.

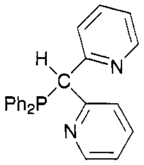
These experiments were performed under similar reaction conditions to those used by Bäckvall and coworkers with [$RuCl_2(PPh_3)_3$] as catalyst precursor.[4]† The hydrogenation of cyclohexanone into cyclohexanol was nearly instantaneous: after 30 s, GC analysis showed 99% conversion. This is a turnover rate of 118 800 h^{-1}, 66 times greater than the initial turnover rate observed by Bäckvall during the first 15 min of the reaction using [$RuCl_2(PPh_3)_3$] as catalyst (only 89% conversion was observed after 1 h).[4] This high activity of **2** is also observed for the hydrogenation of cyclopentanone and acetophenone (Table 1). To the best of our knowledge this is the highest activity ever reported for ruthenium-catalysed transfer hydrogenation of ketones by propan-2-ol.[5] However, as observed for [$RuCl_2(PPh_3)_3$], the activity of **2** for the hydrogenation of propiophenone is low (Table 1).

No activity is observed in the absence of sodium hydroxide and in boiling ethanol the activity is very low (8% conversion after 4 h for the hydrogenation of acetophenone).

It is very likely that the high activity of **2** is related to the presence of the hemilabile ether arm of **1**. Indeed, the complex



1



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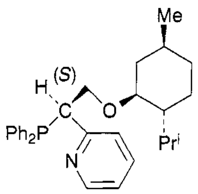
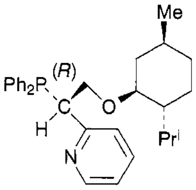


4a



4b

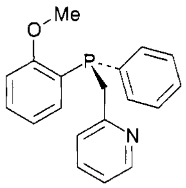


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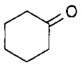
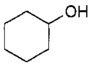
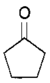
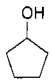
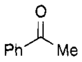
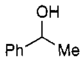
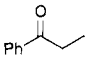
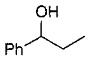
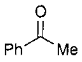
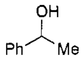
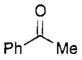
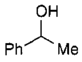
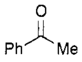
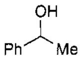
Table 1 Catalysed transfer-hydrogenation of ketones[a]

Catalyst	Substrate	Product	Conversion (%)[b]	Time[b]	Turnover/h^{-1}
2			99 (89)	30 s (1 h)	118 800
2			41 (50) 93	30 s (1 h) 15 min	49 200 3 720
2			50 (48) 88 (75)	30 s (1 h) 15 min (6 h)	90 000 3 520
2			12 (18)	1 h (1 h)	120
6a			82	20 min	2 460
6b			85	20 min	2 550
7			83	1 min	49 800

[a] All the experiments were run on a 10 mmol scale. [b] Values in parentheses refer to results from ref. 4.

$[RuCl_2(PPh_3)(\mathbf{3})]^2$ [**3** = $Ph_2PCH(2\text{-pyridyl})_2$] in which **3** is (P, N, N) bound, is less active for the transfer hydrogenation of acetophenone (45% conversion after 3 h), and the complex $[RuCl_2(PPh_3)(CO)(\mathbf{1})]$ in which **1** is (P, N) bound effects only a 17% conversion after 1 h.

The high efficiency of **2** for hydrogenation of acetophenone led us to check whether optically active tridentate (P, O, N) ligands similar to **1** can induce asymmetric hydrogen transfer reactions.[5,6] The two diastereoisomers of 1-(diphenylphosphino)-2-(1*R*, 2*S*, 5*R*)-menthoxy-1-(2-pyridyl) ethane (**4a** and **4b**) and the donor (*S*)[(phenyl)(2-anisyl)phosphino](2-pyridyl) methane **5** (Scheme 1) have been synthesized, and the corresponding complexes $[RuCl_2(PPh_3)(L)]$ prepared (**6a**, L = **4a**; **6b**, L = **4b**; **7**, L = **5**).[3] Disappointingly, in no case was a significant e.e. observed, even though the activities of the three catalysts were at least as high as that of **2** (Table 1).

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Footnotes

† Typical procedure for catalytic reactions. Degassed propan-2-ol (5 ml) was added to catalyst (0.01 mmol) under nitrogen and the mixture heated at reflux (10 min). Ketone (10 mmol) was dissolved in degassed propan-2-ol (3 ml) and was added dropwise to the refluxing mixture and after 10 min a solution of NaOH (9.5 mg, 0.237 mmol) in propan-2-ol (2 ml) was added dropwise. The mixture was kept at 82 °C and the progress of the reaction monitored by GC analysis.

References

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