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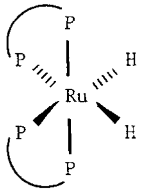
CATALYTIC ASYMMETRIC HYDROGENATION OF α-β-UNSATURATED KETONES USING CHIRAL RUTHENIUM HYDRIDE COMPLEXES.

Viviane MASSONNEAU, Paul LE MAUX and Gérard SIMONNEAUX*
Laboratoire de Chimie des Organométalliques associé au C.N.R.S.,
Université de Rennes I, Campus de Beaulieu, 35042 Rennes, France.

SUMMARY : Chiral ruthenium hydrides : $HRuCl(TBPC)_2$ and $H_2Ru(TBPC)_2$ catalyse the hydrogenation of α-β-unsaturated ketones to ketones (e.e. 62 %).

Asymmetric hydrogenation of prochiral olefins in the presence of chiral rhodium catalyst is now a useful preparative tool for many α-aminoacids[1]. In contrast very little is known about catalytic asymmetric hydrogenation of α,β-unsaturated ketones. Although a few examples using rhodium[2], ruthenium[3] and cobalt[4,5] complexes have been reported, efficient asymmetric catalytic routes for the preparation of optically active ketones still do not exist. We previously reported the first asymmetric hydrogenation of cyclic enones using cobalt carbonyl catalysts[5], we now want to show that good optical yield (ee > 60 %) may be obtained by the hydrogenation of cyclohexenones with new chiral ruthenium hydrides[6].

We have synthesized both monohydride and dihydride ruthenium (II) complexes containing the trans-1,2 bis (diphenylphosphinomethyl) cyclobutane ligand (TBPC) : cis $H_2Ru(TBPC)_2$ 1 and trans $HRuCl(TBPC)_2$ 2. Both complexes were made from $(RuCl_2COD)_n$ using the olefin-phosphine exchange method. However only the monohydride species containing a chlorine ligand has been found effective for catalytic hydrogenation of α,β-unsaturated ketones under mild conditions (50-80°C) (table 1). Small amount of alcools (< 10 %) were also produced. The highest stereoselectivity was obtained with the hydrogenation of isophorone (ee : 62 % ; entry 2). To the best of our knowledge, this stereoselectivity is among the highest for the catalytic asymmetric hydrogenation of α,β-unsaturated ketones[7]. A lower selectivity was observed in the hydrogenation of 3-methyl and 2-methyl 2-cyclohexenones and of α-methylene tetralone. Interestingly, hydrogenated ketones bearing a chiral carbon in the α-position relative to the carbonyl group were found to be optically active in contrast to our previous results obtained with chiral cobalt catalysts[5] (entries 5 and 7).



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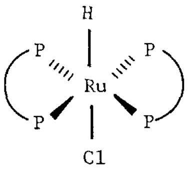

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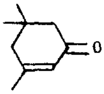
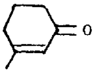
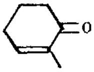
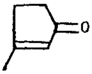
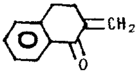
Table 1. Asymmetric hydrogenation catalysed by $HRuCl(TBPC)_2$ (a)

Entry	Substrate	Product ketone configuration $\vert\alpha\vert_D^{25}$	Yield %	% ee (b)	Time (h)	Temperature (°C)
1		R (-4.0°)	25	40	24	80
2	-	R (-6.4°)	20	62	45	50
3 (c)	-	R (-2.8°)	58	27	20	100
4		R (+2.9°)	40	22	22	80
5		S (+3.9°)	38	26	22	80
6		R (+6.4°)	70	4.5	8	80
7		R (+1.2°)	100	23	24	50

[a] 40 atm H_2, 50/1 substrate/catalyst, solvent benzene. [b] The enantiomeric excess is determined on the basis of published values for the optically pure compounds : see ref. 5. [c] $H_2Ru(TBPC)_2$.

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