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LETTER

Ir(I) Complexes with Chiral Terdentate NNN Donor Ligands: Very Effective and Selective Catalysts in Hydrogen Transfer Reactions

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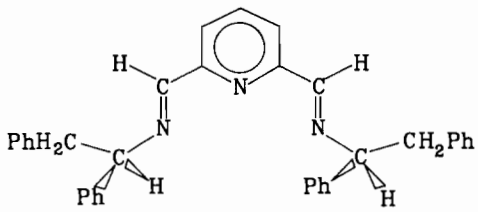
Iridium(I) complexes with bidentate nitrogen donor ligands are very active catalysts in hydrogen transfer reactions from alcohols to several unsaturated organic substrates [1–3]. Tetracoordinated and pentacoordinated chiral Ir(I) derivatives of the type $[Ir(NNR^*)(COD)]ClO_4$ (**I**) and $[Ir(NNR^*)(COD)I]$ (**II**) (COD = *cis,cis*-1,5-cyclooctadiene; NNR* = chiral Schiff base, obtained by condensation of pyridine-2-aldehyde with a primary optically active amine) promote the reduction of prochiral ketones to the chiral alcohols with good optical yields [4, 5].

Rhodium(I) complexes with the same chiral Schiff bases are also active and selective species in transfer hydrogenation [6] and in hydrosilylation of prochiral ketones [7].

The results obtained with complexes **II** [5] pointed out that the catalyst is active even if the non-participative ligands hold three coordination sites. This fact suggested that terdentate chiral chelating ligands could be used instead of bidentate ones. Among the possible terdentate ligands [8–11] we selected those obtained by condensation from pyridine-2,6-dialdehyde (2,6-PDA) and a primary optically active amine, in analogy to bidentate ligands previously reported. The chiral starting material is easily available in both antipodes.

The terdentate chelating ligands have two configurationally stable chiral centres, a C_2 symmetry and offer the advantages to give complexes in which the number of geometrical isomers is considerably low and the free coordination sites are equivalent, being always close to one of two chirality inducing centres. Complexes with such ligands, if still catalytically active, might allow reactions more enantioselective than those performed with the corresponding derivatives with parent bidentate ligands to be obtained.

In this preliminary communication we wish to report that the *in situ* system $[Ir(COT)_2Cl]_2$ + (*R,R*)PDPBI (Scheme 1) ((*R,R*)PDPBI = 2,6-pyridine-



Scheme 1.

1,2-diphenylethyldiimine; see 'Experimental') is surprisingly a very effective catalyst in hydrogen transfer reaction from propan-2-ol to acetophenone ($\bar{\gamma}_{0-5}$ = 102 cycles/min; $\bar{\gamma}_{0-5}$ = average rate between 0 and 5 min) and to unsaturated ketones in the presence of KOH as cocatalyst.

Table 1 (runs 1, 2) shows that the system with the terdentate ligand is more active than the corresponding one with the parent bidentate (*R*)PPBI ligand ((*R*)PPBI = 2-pyridinal-1,2-diphenylethylimine [4]) in the reduction of acetophenone ($\bar{\gamma}_{0-5}$ = 34 cycles/min). Under the same experimental conditions, $[Ir(COT)_2Cl]_2$ alone is totally inactive (run 3) and addition of pyridine-2,6-dialdehyde does not significantly increase the activity (run 4).

TABLE 1. Reduction of acetophenone with propan-2-ol

Run	Precursor	Conversion (%)	Time (min)	e.e. (%)
1	$[Ir(COT)_2Cl]_2$ + (*R,R*)PDPBI	96	15	20.0 *S*(−)
2	$[Ir(COT)_2Cl]_2$ + (*R*)PPBI	45	15	14.0 *S*(−)[a]
3	$[Ir(COT)_2Cl]_2$	1	60	
4	$[Ir(COT)_2Cl]_2$ + 2,6-PDA	4	60	

Reaction conditions: $[Ir(COT)_2Cl]_2 = 0.8 \times 10^{-4}$ M; $[DH_2]/[sub.] = 81.5$; $[sub.]/[Ir] = 1000$; $[KOH]/[Ir] = 2.0$; H_2O(vol.%) = 0.1; [chel]/[Ir] = 1.0; T = 83 °C. [a]Determined at conversion = 96%.

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TABLE 2. Reduction of unsaturated ketones by propan-2-ol. Precursor: $[Ir(COT)_2Cl]_2$ + chelate

Chelate	Substrate	Time (min)	Conversion (%)	Sel.[a] (%)	e.e. (%)
(*R,R*)PDPBI	4-phenyl-3-buten-2-one	120	90	93	67.0 *S*(−)
(*R,R*)PDPBI	4-phenyl-3-buten-2-one	45	43	94	82.0 *S*(−)
(*R*)PPBI	4-phenyl-3-buten-2-one	390	88	76	17.0 *S*(−)
(*S,S*)PDPBI	6-methyl-5-hepten-2-one	135	91	100	13.0 *S*(+)

Reaction conditions: see Table 1; H_2O(vol.%) = 2.0. [a]Selectivity in unsaturated alcohol = unsaturated alcohol(%)/conversion(%).

On the other hand the optical yield is rather low (20.0 e.e.%) and only slightly better than that obtained with the corresponding bidentate ligand (14.0 e.e.%).

High optical yields were instead obtained using 4-phenyl-3-buten-2-one (benzylideneacetone) as substrate. We found that this substrate is reduced with good activity and high chemio- and enantioselectivity: in fact the corresponding *S*(−) allylic alcohol is obtained in 93% yield and with an enantiomeric excess of 67.0% (Table 2). Optical yield up to 82.0% e.e. is reached when the reaction is stopped at 50% conversion.

Using the terdentate (*R,R*)PDPBI ligand, the rate, selectivity and, in particular, enantioselectivity are clearly higher than those observed with the corresponding bidentate (*R*)PPBI ligand. Since both antipodes of the ligand are available, using the (*S,S*) isomer, *R*(+) unsaturated alcohol is obtained with the same rate, yield and enantiomeric excess.

Only a few examples of catalytic systems are reported for the selective formation of unsaturated alcohols by reduction of α,β unsaturated ketones in hydrogenation [12, 13] or in hydrogen transfer reactions [2, 14]; to the best of our knowledge, this is the first example of catalytic highly chemio- and enantioselective reduction of an α,β unsaturated ketone to the optically active allylic alcohol.

In Table 2 is also reported the chemiospecific reduction of 6-methyl-5-hepten-2-one to the corresponding unsaturated alcohol (sulcatol), an economically important pheromone [15]. Our catalytic system allows sulcatol to be obtained in 100% yield; the optical purity is low (13.0 e.e.%), but close to that of the natural product (30% e.e. in *S* isomer).

Further increases of chemio- and enantioselectivity could probably be achieved by changing the substituents at the chiral centres of the ligand and performing the reactions at a lower temperature.

Experimental

Pyridine-2,6-dialdehyde (2×10^{-3} mol) was dissolved in 10.0 ml of ethanol (95%) and, after addition of 5 drops of glacial acetic acid, was treated with 4×10^{-3} mol of *R*(−) or *S*(+) 1,2-diphenylethylamine, obtained by optical resolution of (±) amine, as described in ref. 16. The system was heated under reflux for 40 min and the white product which precipitated by cooling at room temperature was collected, washed with absolute ethanol and dried *in vacuo* at r.t. Crystallisation was from absolute ethanol.

(*R,R*)PDPBI: m.p. = 126 °C, $[\alpha]^{23}_D$ = +196.0 (*c* = 0.5 acetone). *Anal.* Calc. for $C_{35}H_{31}N_3$: C, 85.16; H, 6.33; N, 8.51. Found: C, 83.9; H, 6.14; N, 8.34%. ^{1}H NMR: ($CDCl_3$, TMS int., 200 MHz) δ = 3.24 (d, 4H), δ = 4.56 (t, 2H), δ = 7.06–7.47 (m, 2OH) δ = 7.78 (t, 1H), δ = 8.09 (s, 2H), δ = 8.12 (d, 2H).

(*S,S*)PDPBI: m.p. = 127 °C; $[\alpha]^{23}_D$ = −198.0 (*c* = 0.5 acetone). *Anal.* Calc. for $C_{35}H_{31}N_3$: C, 85.16; H, 6.33; N, 8.51. Found: C, 84.3; H, 6.57; N, 7.79%.

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