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ASYMMETRIC HYDROFORMYLATION OF STYRENE

ON AMINOPHOSPHINEPHOSPHINITES MODIFIED PLATINUM CATALYSTS

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Summary : Pt(II)-aminophosphinephosphinite complexes catalyze the asymmetric hydroformylation of styrene. (S)-2-phenylpropanal with an ee of 48 % is obtained using the simple Pt(ProNOP)Cl_2-$SnCl_2$ combination.

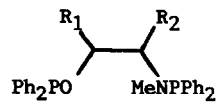
In asymmetric hydroformylation, as in many other transition metal complexes catalyzed reactions, most of the work has been devoted to understand the mechanism of asymmetric induction and the improvement of the catalyst's performance through designing more and more sophisticated chiral ligands [1,2,3].

We describe here the use of a new series of ligands, the mixed aminophosphinephosphinites[4,5] AMPP*, very easily available from natural aminoacids and aminoalcohols, in the asymmetric platinum-tin catalyzed hydroformylation of styrene :

$$Ph\text{-}CH{=}CH_2 + CO + H_2 \xrightarrow[P,T]{PtL_2^*Cl_2\text{-}SnCl_2} \begin{matrix} Ph\overset{*}{C}H(CHO)Me \text{ 2-phenylpropanal} \\ + \\ PhCH_2CH_2CHO \text{ 3-phenylpropanal} \\ + \\ PhEt \text{ ethylbenzene} \end{matrix}$$

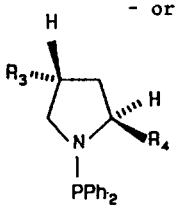
These ligands, having one or two chiral centers, are classified according to their structure[5] :

- acyclic



R_1 = H	R_2 = Me	(S)-AlaNOP	1
"	= iPr	(S)-ValNOP	2
"	= iBu	(S)-LeuNOP	3
"	= Ph	(S)-GlyNOP	4
"	= CH_2Ph	(S)-PheNOP	5
R_1 = Ph	= Me	(1R,2S) EPHOS	6

- or cyclic



R_3 = H	R_4 = CH_2OPPh_2	(S) ProNOP	7
R_3 = $OPPh_2$	R_4 = CO_2Et	(2S,4R) E-ProNOP	8
R_3 = "	R_4 = CO^nBu	(2S,4R) Bu-ProNOP	9
R_3 = "	R_4 = $CO(CH_2)_2$-OEt	(2S,4R) E,E-ProNOP	10

Experimental

$PtL^*_2Cl_2$ complexes were synthesized by addition of an excess of chiral ligand L^*_2 to a solution of Zeise's salt $K[Pt(C_2H_4)Cl_3]$ in acetone.After purification, these are characterized by IR and ^{31}P NMR.

The reactions were conducted in a magnetically stirred and double-walled 50 mL stainless steel reactor. Was sucessively introduced : the cocatalyst $SnCl_2$, $2H_2O$ (0.21 mmol), the platinum complex (0.07 mmol), benzene (10 mL), styrene (10 mmol) and the internal standard (n-decane). The autoclave was sealed, pressurized to 130b with CO/H_2 (1/1) and heated to 80°C. After 4 h the reactor was cooled, depressurized and the mixture distilled in vacuo. The ee's were determined according to literature methods.[6]

Results

The results summarized in Table 1 show that the activity of the different AMPP-modified platinum complexes is lower than the "DIOP- Platinum" one (entry 11).

However, the ee's achieved in these reactions are higher : in some cases (L-EPHOS, entry 6 and ProNOP, entry 7), ee's of up to 30 % are obtained.

In the case of acyclic ligands (entries 1 to 5), as in the cyclic series (entries 7 to 10), the structure variations play an important role in the chirality transfer. Indeed, when R_2 and R_4 are alkyl (entries 1 to 3) or heteroatom containing radicals (entries 8 to 10), one can observe that the measured enantiomeric excess increases when the steric hindrance increases. This effect can be interpreted by considering the different possibilities of conformational mobility given to the isopropyl or isobutyl radicals. The rigidity of the complex during the chirality determining step, which is one of the required conditions for good chirality transfer, is then reduced. This was observed during asymmetric hydrogenations on rhodium catalysts with the same ligands[7].

Substitution of an alkyl by and aryl radical (entries 4 and 5) leads also to a large decrease in the performances of the catalysts. As previously described[8,9], this can be attributed to interactions between the aromatic rings bound to the chelating phosphorus and to the chiral center. These interactions, by increasing the repulsion between the aromatic rings, modify the conformational equilibrium of the complex and thus, reduce the enantioselectivity of the catalysts.

Table 1 : PtL_2^*-$SnCl_2$ catalyzed asymmetric hydroformylation of styrene[a]

Entry	Ligand		Conv[b] %	S ald[c] %	S Etbz[d] %	b/n[e]	ee %	Conf.
1	(S)-AlaNOP	**1**	68	95	5	0.75	23.9	S
2	(S)-ValNOP	**2**	80	96	4	1.06	14.2	S
3	(S)-LeuNOP	**3**	85	96	4	0.96	4	S
4	(S)-GlyNOP	**4**	72	97	3	0.99	1.9	S
5	(S)-PheNOP	**5**	57	95	5	0.89	0.6	S
6	(1R,2S)EPHOS	**6**	54	92.5	7.5	0.70	36.3	S
7	ProNOP[f]	**7**	99	94.5	5.5	0.64	31.9	S
8	E-ProNOP	**8**	57	92	8	0.86	16.5	R
9	E,E-ProNOP	**9**	75	93	7	1.01	11.8	R
10	Bu-ProNOP	**10**	25	95	5	1.06	0.35	S
11	(R,R)-DIOP[g]		100	85.5	14.5	0.64	18	S
12	ProNOP[h]	**7**	70	97	3	0.70	48.1	S
13	ProNOP[i]	**7**	20	92.2	7.5	0.69	46	S
			40	91.5	8.5	0.72	41	S
			82	93.5	6.5	0.74	36	S

[a]See experimental part for standard conditions. [b]Styrene conversion, mol%. [c]Aldehyde selectivity, mol%. [d]Ethylbenzene selectivity, mol%. [e]Branched to linear aldehyde ratio. [f]Reaction time = 100 min. [g]Reaction time = 20 min. [h]Olefin/Sn/Pt = 95:1:1 ; P = 162.5 bar; H_2/CO = 1.5 ; T = 50°C ; t = 36 h. [i]Same conditions as for run 12, except T = 60°C, at different conversions.

A complete study concerning the influence of the reactions conditions (T°, CO and H_2 pressure) and of the reagents concentrations (substrate, catalyst, ligand and cocatalyst) show that, on a ProNOP modified system, the enantioselectivity could be enhanced by working at a low temperature, with a high syngas pressure (and a H_2/CO ratio up to 1) and with L_2^*/Pt and Sn/Pt ratio near to 1. Under the conditions described for entry 12, the enantiomeric excess for (S)-2-phenylpropanal has been held to 48 % at 70% conversion.

Finally, as a recent publication in this field has shown that a racemization process could occur on platinum catalysts[3], we have checked this possibility by taking aliquot portions of the solution at different time for the same reaction (run 13). The results clearly indicate that this process also occurs on our systems and therefore, it is highly probable that upon using methyl orthoformate, the above results could be enhanced by rapid acetalisation of the aldehyde prior to racemization.

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