Tetrahedron Letters,Vol.30,No.42,pp 5759-5762,1989
Printed in Great Britain

0040-4039/89 $3.00 + .00
Pergamon Press plc

UNUSUAL, LINEAR REGIOSELECTIVE HYDROFORMYLATION ON PtL_2Cl_2-IRON OR TIN CATALYSTS

by Sylvain MUTEZ, Eric PAUMARD, André MORTREUX and Francis PETIT

Laboratoire de Chimie Organique Appliquée associé au CNRS,
ENSC Lille, UST Lille Flandres Artois
BP 108 59652 VILLENEUVE D'ASCQ -FRANCE-

***Summary** : PtL_2Cl_2-iron or tin catalysts (L_2 = diphenylphosphinobutane, DIOP...) are found to be highly selective into linear aldehydes during olefin hydroformylation, with up to 90% into hydrocinnamaldehyde and 98% into n heptanal from styrene and 1-hexene, respectively.*

The olefin hydroformylation reaction has been the subject of numerous studies[1,2], and several transition metal complexes are known to catalyze this reaction[3]. Although the most commonly used catalysts are based on cobalt and rhodium, it has been found that Pt^{II}-Sn^{II} combinations were also efficient for this reaction[4].

We describe here the synthesis of new platinum based catalytic systems for which a large enhancement in linear regioselectivity is observed :

$$RCH{=}CH_2 + CO + H_2 \xrightarrow[P,T°]{\substack{PtL_2Cl_2 \\ + \text{ cocatalyst}}} \underset{b}{RCH(CHO)CH_3} + \underset{n}{RCH_2CH_2CHO}$$

To this end, we have imagined that a possible path for the chloride abstraction in PtL_2Cl_2-Sn system can be provided by the electrochemical reduction of PtL_2Cl_2 complexes in an undivided cell according to

$$\text{Cathode} \quad PtL_2Cl_2 + 2e^- \longrightarrow \text{"}PtL_2\text{"} + 2Cl^-$$
$$\text{Anode} \quad Sn \longrightarrow Sn^{++} + 2e^-$$

instead of the use of the $SnCl_2$ Lewis acid.

This process is performed in a glass electrochemical cell, into which are introduced successively 20 ml of propylene carbonate and 10 ml of benzene. 64 mg ($8.66\ 10^{-2}$ mmol) of $Pt(DIOP)Cl_2$[5] are added and the cylindrical electrodes (platinum gauze as the cathode and tin or iron foils as the anode) are introduced in the solution. The electrolysis is then performed under controlled cathodic potential (E = -1,75V vs Ag/AgCl) in order to reduce the platinum complex, previously shown to be reducible at -1,6V according to voltamperometric studies. After consumption of the required amount of electron mole to solubilize the tin or iron cation, the current is stopped[6]. The resulting mixture is then introduced under nitrogen into a stainless steel autoclave, as well as the olefin (either styrene **1**, 8.66 mmol, or 1-hexene **2**, 43.3 mmol). The reactor is then pressurized under CO/H_2 (1:1) at 100atm and heated to 90°C.The results are summarized in table 1.

TABLE 1 : Olefin hydroformylation on $Pt(DIOP)Cl_2$-Sn or Fe catalysts[*]

Run	Substrate (Substrate/ Catalyst)	Cocatalyst	R^{tion}time[#] (h)	alcane mol %	n aldehyde mol %	n/b ratio
1	**1** (100)	$SnCl_2, {}_2H_2O$	5	22	53.5	2.2
2	**1** (100)	Sn, e^-	7	8	73.5	4
3	**1** (100)	Fe, e^-	10	3	80.5	5
4	**1** (100)	Fe, e^-[@]	7	0	90	9
5	**2** (500)	$SnCl_2, {}_2H_2O$	2	20	52	1.9
6	**2** (500)	Sn, e^-	4	7.2	86.5	57[Φ]

[*] Conditions : see text. [#] Time required for a 100 % conversion. [@] Preatreatment of the electroreduced solution is performed with CO/H_2 before introduction of the substrate. [Φ] Some isomerization into 2-hexene (4.8 %) was found at the end of the reaction.

Although the activity of these systems is lower than that of PtL_2Cl_2-$SnCl_2$ catalysts (entries 1 and 5), it is remarkable that both the chemoselectivity (the hydrogenation is reduced) as well as the regioselectivity into the linear aldehyde are strongly enhanced (entry 6, >98% into n aldehyde). Furthermore, it is also shown that platinum-iron systems are as effective as the known platinum-tin catalysts, at least in terms of regioselectivity during styrene hydroformylation[7] (runs 3 and 4).

As indicated, the reactions were conducted in a benzene-propylene carbonate mixture in each case. The choice of propylene carbonate as cosolvent was previously made to enhance the conductivity of the solution for the electrolysis, but appears also to be critical. Indeed, with the electrogenerated $Pt(DIOP)Cl_2/Sn/e^-$ catalysts, the selectivities during styrene hydroformylation change drastically with the propylene carbonate/benzene ratio, as shown in table 2.

TABLE 2 : Solvent effect during styrene hydroformylation over Pt(DIOP)Cl_2/Sn/e^- catalyst *.

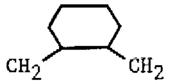
Propylene Carbonate(vol%)	8	20	40	50	60	92
Conv.%	60	58	67	61	53	17
PhEt (mol%)	15	10.5	6	6.5	4	0.2
Ph$(CH_2)_2$CHO (mol%)	53	60	76	76.5	81	89

*Solvent = 25ml ; Pt(DIOP)Cl_2/Sn/Styrene = 1/2.5/100 ; P_{CO} = P_{H2} = 25atm ; T : 80°C ;t = 24h.

The same behaviour is observed with ethylene carbonate, but not with other acyclic alkylcarbonates, whose dielectric constant is much lower.

Furthermore, the activity and selectivity are strongly dependent upon the ligand structure (table 3).

TABLE 3 : Ligand effect during styrene hydroformylation over PtL_2Cl_2/Sn/e^- catalysts*. Pt(PPh_2-X-PPh_2)/Sn/e^-

X	CH_2	$(CH_2)_2$	$(CH_2)_3$	$(CH_2)_4$		DIOP
Conv.(%)	6	27	30	25	100	100
R^{tion}time(h)	20	17	16	24	4	5
PhEt (mol.%)	18	47	20	4	7	7
Ph$(CH_2)_2$CHO (mol.%)	39.5	07	34.5	72	73	73.5

*Solvent = 15ml C_6H_6 + 10ml propylene carbonate ; PtL_2Cl_2/Sn/Styrene = 1/2.5/100 ; P_{CO} = P_H = 50atm ; T : 50°C.

These results indicate that the nature of the solvent and ligand are critical in these reactions : most probably, dissociated platinum complexes are responsible for this unexpected regioselectivity, the role of tin or iron being to abstract chloride anions to produce cationic platinium species. The presence of bulky, highly strained chelating ligands is also required, as previously shown on PtL_2Cl_2-$SnCl_2$ combinations[8]. Finally, the high regioselectivity observed with iron prompted us to study Pt(DIOP)Cl_2-"Fe" combinations in which the cocatalyst is in a formal +2 or +3 oxidation state. With styrene, the hydrocinnamaldehyde/hydratropaldehyde ratio is enhanced to 12.4 and 13.6 with Fe_2O_3 and Fe_3O_4 as cocatalysts in a benzene-propylene carbonate mixture (20/5)[9].

These new results provide further evidence for the usefulness of electrochemistry in its application to the synthesis of unusual homogeneous catalytic species[10], which in this case has allowed to find out new Platinum-Iron systems for unprecedented regioselective hydroformylation of styrene into linear aldehyde.

References

1. O. Roelen, Angew. Chem., 1948, **7**, 213.
2. R.L. Pruett, Adv. Organomet. Chem., 1979, **17**, 1.
3. I. Ojima, K. Kato, M. Okabe and T. Fuchikami, J. Amer. Chem. Soc., 1987, **109**, 7714.
4. I. Schwager and J.F. Knifton, J. Catal., 1976, **45**, 256.
5. DIOP=2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane.
6. The metal consumption fits exactly with the solubilization of one tin or iron atom per platinum, when 2 electron mole have passed.
7. C.Y. Hsu and M. Orchin, J. Amer. Chem. Soc., 1975, **97**, 3553.
8. Y. Kawabata, T. Hayashi and I. Ogata, J. Chem. Soc. Chem. Commun., 1979, 462.
9. Conditions : Styrene/Pt/Fe=100/1/1 ; $P_{CO}=P_{H2}$=50Atm ; T°=90°C ; Conv.=100% after 18^h.
10. A. Mortreux and F. Petit, Appl. Catal., 1986, **24**, 1.

(Received in France 29 May 1989)