Electrochemical Synthesis of Dimeric Platinum Hydride Species Responsible for Highly Regioselective Alkene Hydroformylation

Eric Paumard, André Mortreux, and Francis Petit

Laboratoire de Chimie Organique Appliquée, UA CNRS 402, ENSC Lille, UST Lille Flandres Artois, BP 108 59652 Villeneuve D'Ascq, France

 PtL_2Cl_2 complexes (1) [L₂ = diop, 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane] have been used as catalyst precursors for alkene hydroformylation after electroreduction using a soluble tin or iron anode, followed by treatment with carbon monoxide-hydrogen; the remarkable regioselectivities for linear aldehyde formation (*ca.* 98% from hex-1-ene and 90% from styrene) are explained by the production of chelated, bridged platinum hydride cationic species [L₂Pt(H)(μ -L₂)Pt(H)L₂]²⁺, stabilized by the presence of a polar, highly dissociating solvent.

Alkene hydroformylation is the most important homogeneous catalytic feaction for producing aldehydes, using cobalt, rhodium, and platinum based catalysts.^{1,2}

For the bimetallic platinum-tin system,³ several species have been isolated from the reaction mixture.⁴ However, the role which the SnCl₂ co-catalyst plays in both activity and selectivity remains an open question.^{5,6}

We describe here the electrochemical synthesis of new platinum species from PtL_2Cl_2 complexes (1) which, after CO/H_2 treatment, afford well defined platinum hydride cationic moieties suggested to be responsible for the very high regioselectivity observed during hex-1-ene and styrene hydroformylation. Thus, a preliminary voltammetric study on the complex $Pt(diop)Cl_2$ (1a)[†] in propylene carbonate-benzene (NBu₄PF₆ as supporting electrolyte) shows a reduction wave at -1.6 V vs. Ag/AgCl. With a tin anode during electrolysis of this complex, Sn^{2+} is generated, so that a new Pt–Sn couple can be produced electrochemically.

In a typical experiment, (1a) (10^{-2} mmol) was introduced in an undivided electrochemical glass cell in propylene carbo-

[†] diop = 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenyl-phosphino)butane.



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Figure 1.32.44 MHz ³¹P{¹H} N.m.r. spectrum of $[Pt_2(H)_2(\mu-diop)(diop)_2]^{2+}$ [SnCl₃-]₂ in C₆D₆-C₆H₆-propylene carbonate (250 K). (SM = starting material; arrows correspond to coupling of P_A by P_B and P_X).



 $\label{eq:Figure 2.400 MHz 1H N.m.r. spectrum of $$ [Pt_2(H)_2(\mu-diop)(diop)_2]^2$ $$ [SnCl_3^-]_2$ in $C_6D_6-C_6H_6$ propylene carbonate (250 K)$. $$ (250 K)$ $$ Comparison of $$ [Pt_2(H)_2(\mu-diop)(diop)_2]^2$ $$ (SnCl_3^-]_2$ in $C_6D_6-C_6H_6$ propylene carbonate (250 K)$. $$ (250 K)$ $$ (250 K)$$



Figure 3. 85.88 MHz ¹⁹⁵Pt{¹H} N.m.r. spectrum of $[Pt_2(H)_2(\mu-diop)(diop)_2]^2+[SnCl_3^-]_2$ in $C_6D_6-C_6H_6$ -propylene carbonate (250 K).

 Table 1. Styrene hydroformylation over (1a) modified chemically or electrochemically.^a

Cocatalyst	<i>t/</i> h	% Con- version	PhEt /mol %	n-Aldehyde /mol %	n/b ratio ^b
$SnCl_2 \cdot 2H_2O$	5	100 100	22	53.5 73.5	2.2
Fe,e ⁻	24	100	3	73.3 87.5	4 9.2
Fe,e ⁻	24	46°	1	90	10

^a See text for conditions. ^b Normal to branched ratio. ^c CO/ $H_2 = 4$.

nate-benzene (25 ml; 40/60). Electrolysis under controlled potential (-1.85 V vs. Ag/AgCl) with cylindrical platinum gauze and cylindrical tin plate electrodes was continued until 2 moles of electrons per platinum atom had passed, which corresponds to the dissolution of one Sn²⁺/Pt. The overall mixture was transferred into an autoclave under nitrogen and styrene (0.9 g, 8.66 mmol) added. Hydroformylation was conducted at 90 °C under CO/H₂ (1/1, 100 bar) and the reaction followed by chromatography. Table 1 compares the results obtained with the classical SnCl₂·2H₂O cocatalyst and also with an iron anode.

These electrochemically reduced catalysts have also been applied to hydroformylation of hex-1-ene; for substrate/catalyst = 500, 98% selectivity for n-heptanal formation was obtained with the Pt–Sn system.

These remarkable regioselectivities prompted us to look at other phosphines in the PtL_2Cl_2 precursors which could replace diop (Table 2).

Obviously, a long methylene chain in the ligand is the key factor governing the regioselectivity for linear aldehyde formation, the activity depending also on the rigidity of the four-membered carbon chain. Such behaviour is in agreement with previous studies on pent-l-ene hydroformylation.⁷

Spectroscopic studies have been performed on the $Pt(diop)Cl_2$ electroreduced solution (obtained with a tin

anode) following treatment with CO/H₂ under 100 atm for 2 h at 90 °C, and also after the catalytic reaction. In both cases, the same spectra were observed (Figures 1—3): (i) the 32.45 MHz $^{31}P{^{1}H}$ n.m.r. spectrum shows the presence of three different phosphorus atoms;‡ (ii) the 400 MHz ^{1}H n.m.r. spectrum reveals the presence of a Pt–H bond;‡ (iii) an octet in the 85.88 MHz $^{195}Pt{^{1}H}$ n.m.r. spectrum‡ indicates the symmetrical nature of the complex, to which structure (A) can be assigned.

The counter-anion was shown by ¹¹⁹Sn n.m.r. spectroscopy (149.21 MHz, -36 p.p.m. vs. SnMe₄) and mass spectrometry to have the SnCl₃⁻ structure.

A similar spectroscopic study on the other complexes shows that only complex (1g) has the same dihydrido structure, whereas complex (1f) does not give well defined spectra. It is also significant that a similar dihydride structure is apparent when an iron anode is used, in which case the anion formed is $FeCl_3^-$, as shown by mass spectrometry.

The 85.88 MHz 195 Pt{¹H} n.m.r. spectrum is centred at -5390 p.p.m. vs. H₂PtCl₆, the $^{1}J_{P.Pt}$ values being equivalent to those from the 31 P n.m.r. spectrum.

[‡] The 32.44 MHz ³¹P{¹H} n.m.r. spectrum can be interpreted as a second order spectrum owing to the proximity of the P_A and P_B chemical shifts (11.5 and 10 p.p.m. vs. H₃PO₄, respectively, 5 p.p.m. for P_X). The ¹J (Pt-P) coupling constants are 2850 Hz for P_A, 2680 Hz for P_B, and 2050 Hz for P_X. The 162 MHz ³¹P{¹H} n.m.r. spectrum gives an ABX system in which the ²J (P-P) coupling constants are measured accurately: ²J(P_A-P_B) = 315 Hz, ²J(P_A-P_X) = ²J(P_B-P_X) = 21 Hz. These values are consistent with a structure in which P_A and P_B.

The 400 MHz ¹H n.m.r. spectrum consists of a series of doublets of triplets: $\delta - 5.2$, ${}^{2}J_{P-H}$ (*trans*) 160 Hz, ${}^{2}J_{P-H}$ (*cis*) 18 Hz [the resolution of this spectrum did not allow the measurement of the second ${}^{2}J_{P-H}$ (*cis*) coupling constant]. This difference in ${}^{2}J_{P-H}$ coupling constants is in agreement with previous results obtained for square planar complexes, where ${}^{2}J_{P-H}$ (*trans*) is always larger than ${}^{2}J_{P-H}$ (*cis*) (J. P. Jesson, in 'Transition Metal Hydrides,' ed. E. L. Muetterties, Marcel Dekker, New York, 1971, p. 75 and ref. therein). The satellite signals are due to 195 Pt–H coupling (${}^{1}J_{P+H}$ 825 Hz). A v_{Pt-H} vibration is also observed at 2010 cm⁻¹ in the i.r. spectrum.

1	.3	8	3

Table 2. Ligand effect on linear aldehyde regioselectivity with cis-PtL₂Cl₂-'Sn' catalysts.^a

Complex	$PtL_2Cl_2 + SnCl_2$				$PtL_2Cl_2/Sn/e^-$			
	t/h	% Conversion	PhEt /mol %	n-Aldehyde /mol %	t/h	% Conversion	PhEt /mol %	n-Aldehyde /mol %
(1b)	24	96	4.5	65	24	3	10	58.5
(1c)	22	30	17.3	48	20	6	18	39.5
(1d)	4	95	37	16	17	27	47	7
(1e)	1.5	100	27	28	16	30	20	34.5
(1f)	1.5	100	17	45.5	24	25	4	72
(1g)	1	100	14.5	43.5	4	100	7	73
(1a)	1	100	20	49.5	5	100	7	73.5

^a Conditions: as for Table 1, except styrene/Pt/Sn = 100/1/2.5; solvent: benzene (25 ml) for PtL₂Cl₂-SnCl₂ and propylene carbonatebenzene (15/10) for PtL₂Cl₂/Sn/e⁻ catalysts. For PtL₂Cl₂-SnCl₂ combinations, experiments in propylene carbonate-benzene mixtures showed no change in regioselectivity with change in propylene carbonate : benzene ratio.

Therefore, we suggest that the bridged dimeric structure of the chelated complex, dissociated by the polar solvent, plays a key role in the regioselective step of this reaction, via steric interaction between the substrate and the ligand in this cage-type structure.

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