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

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PtL_2Cl_2 complexes (**1**) [L_2 = 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 $[L_2Pt(H)(\mu\text{-}L_2)Pt(H)L_2]^{2+}$, stabilized by the presence of a polar, highly dissociating solvent.

Alkene hydroformylation is the most important homogeneous catalytic reaction 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 $SnCl_2$ co-catalyst plays in both activity and selectivity remains an open question.[5,6]

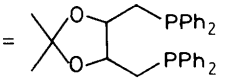
We describe here the electrochemical synthesis of new platinum species from PtL_2Cl_2 complexes (**1**) which, after CO/H_2 treatment, afford well defined platinum hydride cationic moieties suggested to be responsible for the very high regioselectivity observed during hex-1-ene and styrene hydroformylation. Thus, a preliminary voltammetric study on the complex $Pt(diop)Cl_2$ (**1a**)† in propylene carbonate–benzene (NBu_4PF_6 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-

$[PtL_2Cl_2]$

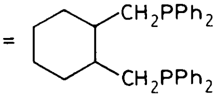
(**1**)

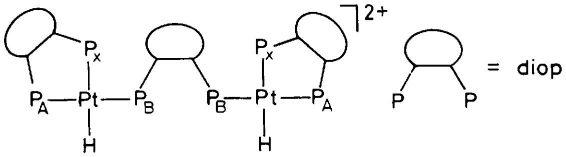
a; L_2 =



b; L_2 = $(PPh_3)_2$
c; L_2 = $PPh_2CH_2PPh_2$
d; L_2 = $PPh_2(CH_2)_2PPh_2$
e; L_2 = $PPh_2(CH_2)_3PPh_2$
f; L_2 = $PPh_2(CH_2)_4PPh_2$

g; L_2 =





(A)

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† diop = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane.

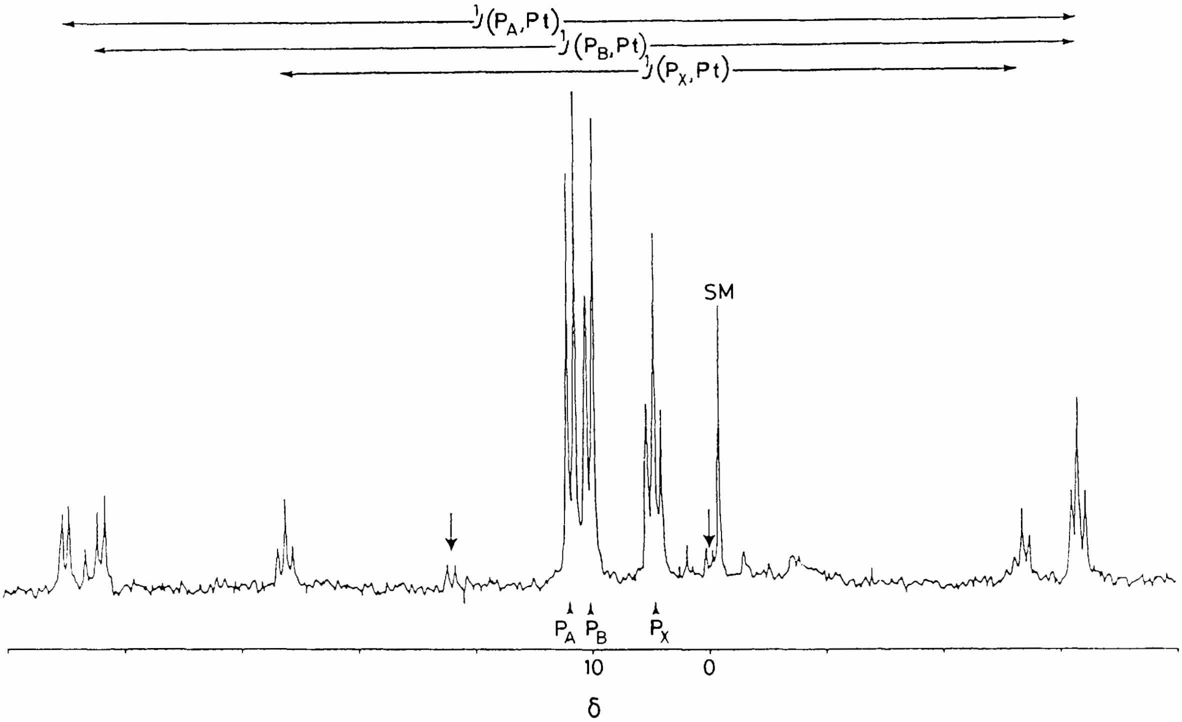

Figure 1.32.44 MHz $^{31}P\{^1H\}$ N.m.r. spectrum of $[Pt_2(H)_2(\mu\text{-diop})(diop)_2]^{2+}$ $[SnCl_3^-]_2$ in C_6D_6–C_6H_6–propylene carbonate (250 K). (SM = starting material; arrows correspond to coupling of P_A by P_B and P_X).

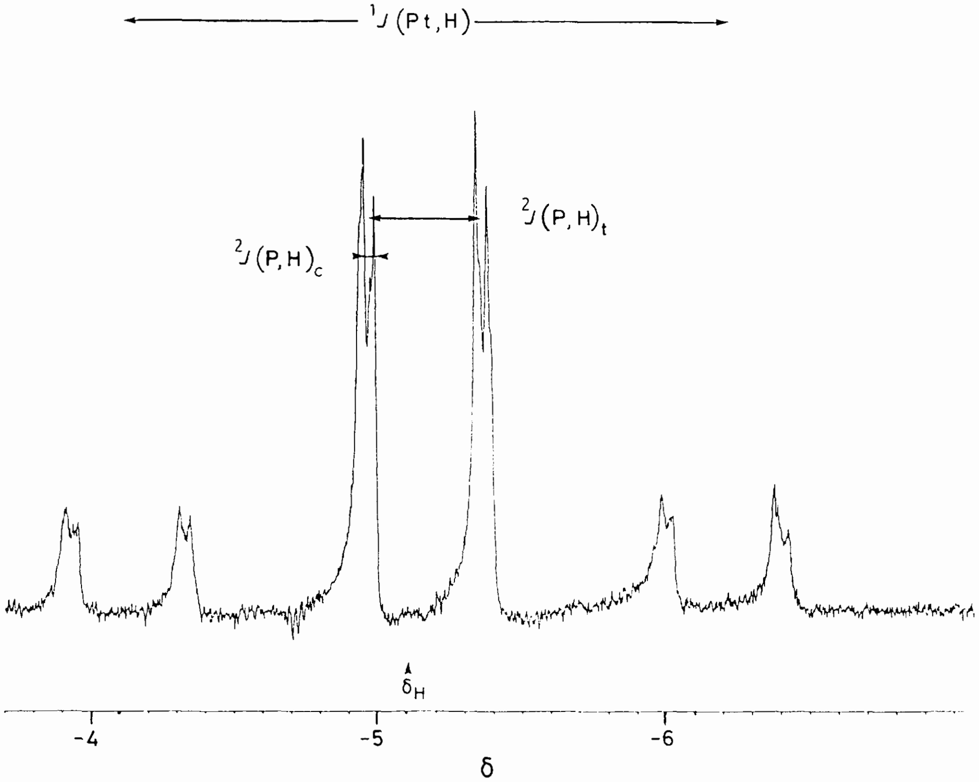

Figure 2. 400 MHz ^1H N.m.r. spectrum of $[Pt_2(H)_2(\mu\text{-diop})(diop)_2]^{2+}$ $[SnCl_3^-]_2$ in C_6D_6–C_6H_6–propylene carbonate (250 K).

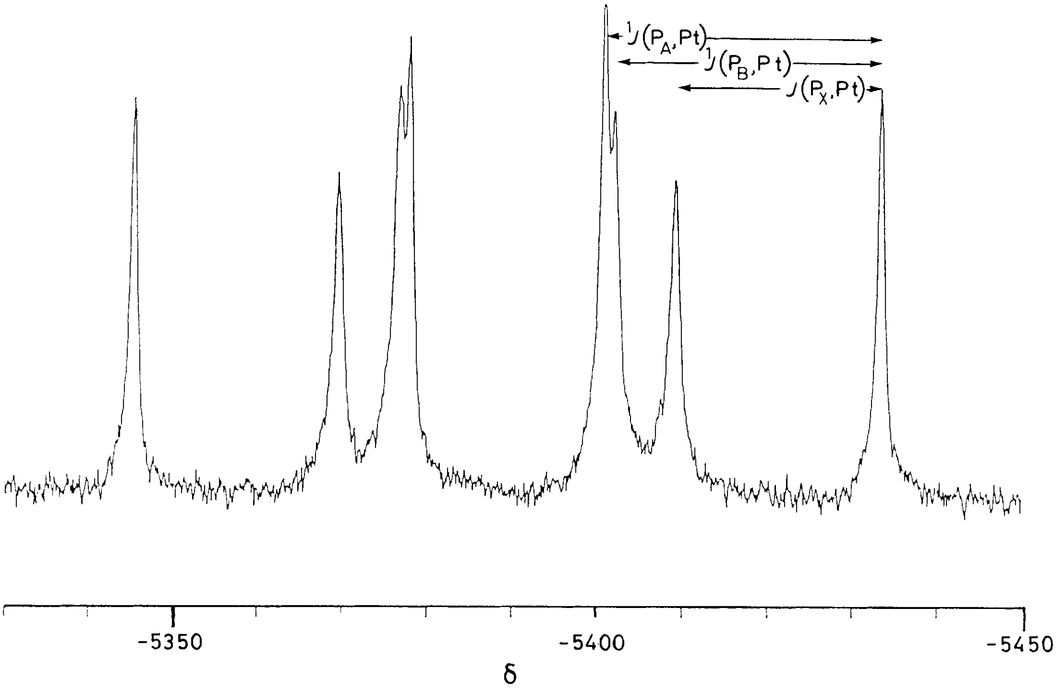

Figure 3. 85.88 MHz $^{195}Pt\{^1H\}$ N.m.r. spectrum of $[Pt_2(H)_2(\mu\text{-diop})(diop)_2]^{2+}[SnCl_3^-]_2$ in C_6D_6–C_6H_6–propylene carbonate (250 K).

Table 1. Styrene hydroformylation over (**1a**) modified chemically or electrochemically.[a]

Cocatalyst	*t*/h	% Conversion	PhEt /mol %	n-Aldehyde /mol %	n/b ratio[b]
$SnCl_2{\cdot}2H_2O$	5	100	22	53.5	2.2
Sn,e$^-$	7	100	8	73.5	4
Fe,e$^-$	24	100	3	87.5	9.2
Fe,e$^-$	24	46[c]	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 Sn^{2+}/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/H_2 (1/1, 100 bar) and the reaction followed by chromatography. Table 1 compares the results obtained with the classical $SnCl_2{\cdot}2H_2O$ 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-1-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/H_2 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 $^{31}P\{^1H\}$ n.m.r. spectrum shows the presence of three different phosphorus atoms;‡ (ii) the 400 MHz ^1H n.m.r. spectrum reveals the presence of a Pt–H bond;‡ (iii) an octet in the 85.88 MHz $^{195}Pt\{^1H\}$ n.m.r. spectrum‡ indicates the symmetrical nature of the complex, to which structure (A) can be assigned.

The counter-anion was shown by ^{119}Sn n.m.r. spectroscopy (149.21 MHz, −36 p.p.m. *vs.* $SnMe_4$) and mass spectrometry to have the $SnCl_3^-$ 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.

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‡ The 32.44 MHz $^{31}P\{^1H\}$ 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.* H_3PO_4, 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 $^{31}P\{^1H\}$ 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 are *trans* to each other and P_X is *cis* with respect to P_A and P_B.

The 400 MHz ^1H n.m.r. spectrum consists of a series of doublets of triplets: δ −5.2, $^2J_{P\text{-}H}$ (*trans*) 160 Hz, $^2J_{P\text{-}H}$ (*cis*) 18 Hz [the resolution of this spectrum did not allow the measurement of the second $^2J_{P\text{-}H}$ (*cis*) coupling constant]. This difference in $^2J_{P\text{-}H}$ coupling constants is in agreement with previous results obtained for square planar complexes, where $^2J_{P\text{-}H}$ (*trans*) is always larger than $^2J_{P\text{-}H}$ (*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 ($^1J_{Pt\text{-}H}$ 825 Hz). A $\nu_{Pt\text{-}H}$ vibration is also observed at 2010 cm^{-1} in the i.r. spectrum.

The 85.88 MHz $^{195}Pt\{^1H\}$ n.m.r. spectrum is centred at −5390 p.p.m. *vs.* H_2PtCl_6, the $^1J_{P\text{-}Pt}$ values being equivalent to those from the ^{31}P n.m.r. spectrum.

Table 2. Ligand effect on linear aldehyde regioselectivity with *cis*-PtL_2Cl_2–'Sn' catalysts.[a]

	$PtL_2Cl_2 + SnCl_2$				$PtL_2Cl_2/Sn/e^-$			
Complex	*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 PtL_2Cl_2–$SnCl_2$ and propylene carbonate–benzene (15/10) for $PtL_2Cl_2/Sn/e^-$ catalysts. For PtL_2Cl_2–$SnCl_2$ 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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