Platinum Hydroformylation Catalysts containing Diphenylphosphine Oxide Ligands

Piet W. N. M. van Leeuwen,* Cornelis F. Roobeek, Richard L. Wife, and John H. G. Frijns

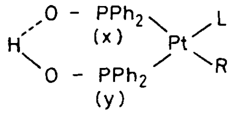
Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B.V.), Badhuisweg 3, 1031 CM, Amsterdam, The Netherlands

Platinum complexes of the general formula $Pt(H)(Ph_2PO)(Ph_2POH)(PPh_3)$ (**1a**) catalyse the hydroformylation of hept-1-ene and, more significantly, hept-2-ene, yielding products of high linearity (90 and 60%, respectively); the intermediate alkyl and acyl complexes (**1c—e**) which most often escape direct observation in a catalytic system, have been successfully isolated and identified.

There is a considerable commercial incentive to obtain linear products from the hydroformylation of internal alkenes. Attempts to improve on the present generation of cobalt catalysts[1a] are aimed specifically at developing more stable catalysts that can be used under milder conditions, give rise to less hydrogenation, and allow easier product separation. The platinum-based catalysts required tin dichloride or trichloride[1b—f] as additives and are only moderately active, affording poor linearities and high alkane makes. We now report on some significant improvements achieved with a platinum–diphenylphosphine oxide system.

The first catalyst was prepared[1g] by mixing $Pt(1,5\text{-cod})_2$, (cod = cyclo-octa-1,5-diene), PPh_3, and Ph_2POH; in hydroformylation it gave rise to a high linearity (>90%; see Table 1) with terminal alkenes (hept-1-ene). The activity varied with the type of phosphine added and the best results were obtained using an *in situ* mixture of $Pt(1,5\text{-cod})_2$, $Ph_2PCH_2CH_2PPh_2$ (dppe), and Ph_2POH. In the absence of diphenylphosphine oxide no activity was observed. From the reaction with PPh_3 as the added ligand we isolated and characterized the known[2] complex (**1a**), which we now report to be an active hydroformylation catalyst.† In contrast to the trichlorostannate catalyst, the present complex (**1a**) catalyses the hydroformylation of internal alkenes (hept-2-ene) yielding an impressive linearity for both the aldehyde (55%) and the corresponding alcohol (hydrogenation) product (73%); however, the alkane make is high as well (17%).

The hydroformylation activity of (**1a**) could be followed stepwise by treating the catalyst with ethene (20 bar, 90 °C), which gave the isostructural platinum–ethyl intermediate (**1c**) (see Table 2). Passing carbon monoxide through the solution (1 bar; 25 °C) smoothly afforded the platinum–acyl (propionyl) complex (**1d**), in what appears to be a much faster reaction than the ethene insertion. With higher alkenes (propene, hept-1-ene) the corresponding platinum–acyl complexes were also obtained (the platinum–alkyls could not be observed in the step prior to CO insertion and only the platinum hydride was recovered). Examination of the ^{31}P n.m.r. spectra of the hydroformylation solution after work-up revealed the exclusive presence of the hydride (**1a**) and the acyl complex (**1d**) (1 : 1 for hept-1-ene). We suggest that the



(**1**)

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† Complex (**1a**) was also found to be active as an alkene hydrogenation catalyst. With ethylene (95 °C, 20 bar, benzene) turnover rates of 200 mmol (mmol cat.)$^{-1}$ h^{-1} were obtained. Hept-1-ene reacted much slower. The effect is very similar to the tin chloride effect on platinum chloride catalysed hydrogenation (ref. 3).

Table 1. Hydroformylation with platinum–diphenylphosphine oxide catalysts.[a]

Catalyst composition (molar ratio)	Pressure/ bar	Time/ h	Substrate	% Conversion (% linearity) C$_8$-aldehydes	C$_8$-alcohols	Heptane	Rate[b]/ mmol (mmol cat.)$^{-1}$ h^{-1}
Pt(cod)$_2$–PPh$_3$–Ph$_2$POH (1 : 1 : 1)	50	1	Hept-1-ene	9.8 (>90)	8.6 (>90)	0.9	18
Pt(cod)$_2$–Ph$_2$POH (1 : 4)	50	1	Hept-1-ene	1.7 (>90)	5.4 (>90)	3.6	7
Pt(cod)$_2$–Ph$_2$POH–dppe (1 : 1 : 1)[c]	50	1	Hept-1-ene	24.0 (>90)	3.1 (>90)	0.9	27
Pt(H)(Ph$_2$PO)(Ph$_2$POH)(PPh$_3$) (**1a**)	45	1.5	Hept-1-ene	7.9 (90)	9.6 (80)	1.2	11
(**1a**)	94	1.5	Hept-1-ene	5.1 (83)	10.3 (91)	1.0	10
(**1a**)	94	2.5	Hept-2-ene	8.1 (55)	5.8 (73)	4.8	5
Pt(H)(Ph$_2$PO)(Ph$_2$POH)$_2$ (**2a**)	30	7	Ethene (20 bar)	Pentan-3-one 2.25 mmol	Propan-1-ol 2.35 mmol		7

[a] Conditions: 0.1 mmol of platinum compound, 20 ml of benzene or toluene, H$_2$–CO molar ratio 2 : 1, 100 ml autoclave, temperature 100 °C, 10 mmol of hept-1-ene or -2-, conversion based on heptene intake. Measured by g.c. on a HP-5840-A instrument with a 12 ft × 1/8 in column (10% Carbowax-20M on HP-chrom WAW-DMS-80-100 mesh), using the solvent as standard after calibration with authentic samples. [b] Rate: average turnover frequency of mmol oxo-product per mmol of catalyst per hour. [c] dppe = 1,2-bis(diphenylphosphino)ethane.

Table 2. ^{31}P and ^{1}H n.m.r. data for catalyst (**1a**) and intermediate (**1b**—**e**) and (**2b**).

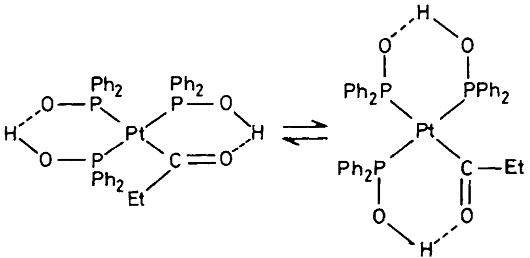
	Compound L	R	δ^{31}P/p.p.m. δL	δP$_x$	δP$_y$	Coupling constants/Hz J(Pt–L)	J(Pt–P$_x$)	J(Pt–P$_y$)	J(L–P$_x$)	J(L–P$_y$)	J(P$_x$–P$_y$)	δ^{1}H
(**1a**)	PPh$_3$	H[c]	23.2	93.0	76.4	2242	2385	2960	17	367	29	−4.3[a] (1H)
(**1b**)	P(p-OMeC$_6$H$_4$)$_3$	Cl[c]	22.1	61.9	73.1	2141	3791	2825	16	416	19	–
(**1c**)	PPh$_3$	Et[b]	24.7	89.3	72.4	2405	1965	3337	18	407	30	+ 0.45 (m, 5H)
(**1d**)	PPh$_3$	COEt[b,e]	18.2	84.2	54.0	2518	1637	3303	23	334	38	+ 1.82 (d, 2H), 0.20 (t, 3H)
(**1e**)	PPh$_3$	COPr^n [c]	19.0	87.0	59.0	2573	1651	3330	23	335	38	+ 1.32 (2H), 0.10 (2H), 0.04 (3H)
(**2b**)	Ph$_2$POH	COEt[c,d]	(76.8)	88.0	(76.8)	(2946)	1739	(2946)	(32.4)	400	(32.4)	+ 1.43 (2H), −0.17 (3H)

[a] J(L–H) 75, J(P$_x$–H) 163, J(P$_y$–H) 25, J(Pt–H) 855 Hz. [b] In C$_6$D$_6$. [c] In CD$_2$Cl$_2$; measured on Bruker WM-250 and WH-90 instruments; integrations (nH) *vs.* phenyl protons. [d] Exchange averaged values at 300 K in parentheses; at 213 K the exchanging nuclei L and P$_y$ appear at δ = 72 and 87 p.p.m. [e] Complex (**1d**) crystallizes according to quantitative g.c. and n.m.r. with two molecules of benzene, and with approximately one mole of water. Satisfactory elemental analyses were obtained.

predominant catalyst entity in hydroformylation is the acyl complex, and that the release of the aldehyde from the acyl complex is rate-determining, with the equilibria as expressed in equations (1)—(3).

$$\begin{array}{lcll} \text{Pt–H} + \text{alk-1-ene} & \rightleftharpoons & \text{Pt–}n\text{-alkyl} & (1) \\ \text{Pt–}n\text{-alkyl} + \text{CO} & \rightleftharpoons & \text{Pt–acyl} & (2) \\ \text{Pt–acyl} + \text{H}_2 & \longrightarrow & \text{Pt–H} + \text{aldehyde} & (3) \end{array}$$

For a comparison of the ligand properties of SnCl$_3^-$ and Ph$_2$PO$^-$ the J(P–Pt) coupling constants of a *trans*-co-ordinated PPh$_3$ may be considered. In complexes (**1a,c**—**e**) the Pt–P(phosphine) coupling constants are small (2000—2500 Hz) compared with the analogous tin complexes (3700—4000 Hz),[4] pointing to significant differences between the *trans* effects of the two ligands. Mechanistically, the influence of the Ph$_2$PO anion may be even more profound than a simple *trans* effect, as is usually invoked for SnCl$_3^-$.‡§



(**2b**)

Both catalytic and structural data may serve as an illustration. When (**1a**) was treated with an excess of Ph$_2$POH the new complex Pt(H)(Ph$_2$PO)(Ph$_2$POH)$_2$ (**2a**) precipitated. Complex (**2a**) was also prepared *in situ* from Pt(cod)$_2$ and Ph$_2$POH and under hydroformylation conditions, produced propan-1-ol and surprisingly pentan-3-one from ethene (Table 1). The best conditions for formation of pentan-3-one were high ethene pressure, low temperatures, and non-alcoholic solvents. Pentan-3-one, not found in other platinum systems, results from ethene insertion into the platinum–carbon bond of the propionyl complex. This reaction has only been observed in the absence of additional phosphine. Work-up of the solution from ethene hydroformylation with (**2a**) indi-

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‡ The role of the trichlorostannate ligand in homogeneous catalysis has been thoroughly studied by several authors. For a recent discussion see the work by H. C. Clark and co-workers (ref. 5) who reject the classical role of the *trans* effect, and instead present evidence to the effect that the role of SnCl$_3^-$ is to provide a good leaving group, equivalent to a small *trans* effect. This reasoning also finds support in the n.m.r. results quoted above (ref. 3, 4a) and in the activity of cationic platinum complexes without SnCl$_3^-$ (ref. 1e).

§ Toniolo and co-workers (ref. 6) stress that the major difference between the platinum–chloro complex [*trans*-PtCl(COPr^n)(PPh$_3$)$_2$] and the trichlorostannate–platinum complex [*trans*-Pt(SnCl$_3$)(COPr^n)(PPh$_3$)$_2$] lies in the final hydrogenation step, since both complexes easily form acyl derivatives under hydroformylation conditions.

cated the presence of a propionyl intermediate (**2b**) (80%), as evidenced by ^1H and ^{31}P n.m.r. spectra. Intramolecular exchange of the two *trans* phosphorus atoms alternatingly bonded through a hydrogen bond to the acyl or phosphine oxide group, gave a temperature-dependent signal broadening, and the Pt coupling was retained. The third phosphorus (*trans* to the acyl group) remained unchanged.

In these experiments we have found an ambident character for the phosphine oxide anion ligand: the soft phosphorus donor atom co-ordinates to platinum while internal bridging by the hard oxygen atom results in a unique co-operation with either the adjacent ligand or the (Pt-)co-ordinated acyl group.

The ambident ligand can also play a dominant role§ in the conversion of the acyl intermediate into the aldehyde product. R_2POH may provide a proton to form the aldehyde, and the resulting platinum phosphine oxide complex seems ideally set up for a heterolytic dihydrogen splitting to regenerate platinum hydride [equation (4)].

$$Pt^{2+}–R_2PO^- + H_2 \longrightarrow PtH^+ + R_2POH \qquad (4)$$

Received, 27th August 1985; Com. 1260

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