# Platinum–Diphosphine–Tin Systems as Active and Selective Hydroformylation Catalysts

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*Summary* The activity of a platinum dichloride–phosphine–tin(II) chloride complex as a hydroformylation catalyst was dramatically enhanced by the use of diphosphine ligands which were capable of forming a strained seven-membered chelate ring; the best ligand was *trans*-1,2-bis(diphenylphosphinomethyl)cyclobutane, which afforded hexanals (n/iso = 99/1) from pent-1-ene with a much higher reaction rate than by the use of $HRh(CO)(PPh_3)_3$.

IT has been reported that the $PtCl_2(PPh_3)_2$–$SnCl_2$ system is a good catalyst for the selective hydroformylation of 1-olefins to n-aldehydes, although it is not as active as rhodium catalysts,[1] and that the activity is reduced by the use of chelating diphosphines such as 1,2-bis(diphenylphosphino)ethane.[2]

We have found, however, that the reaction rate and the selectivity of n-aldehyde formation strongly depend on the methylene chain length of the chelating ligand, $Ph_2P[CH_2]_n$-$PPh_2$, as shown in Figure 1.[3] The rate reached a maximum at $n = 4$ and was further improved by restricting the conformational flexibility of the $n = 4$ methylene chain by introducing a ring structure into the chain as shown in the Table. Thus, the platinum complex containing $(DP)_2$, which has a rigid cyclobutane skeleton, was more active and more selective to n-aldehyde formation than $HRh(CO)(PPh_3)_3$ (compare run 6 *vs.* 7 and 8 *vs.* 9). Excess of phosphine retards the reaction, and the maximum rate was observed at P/Pt = *ca.* 3 (atomic ratio) when using $(DP)_2$. Hydrogenation and isomerization of 1-olefins could be depressed by lowering the reaction temperature (compare runs 6 and 8) and controlling the CO and $H_2$ pressure (compare runs 4 and 5).†

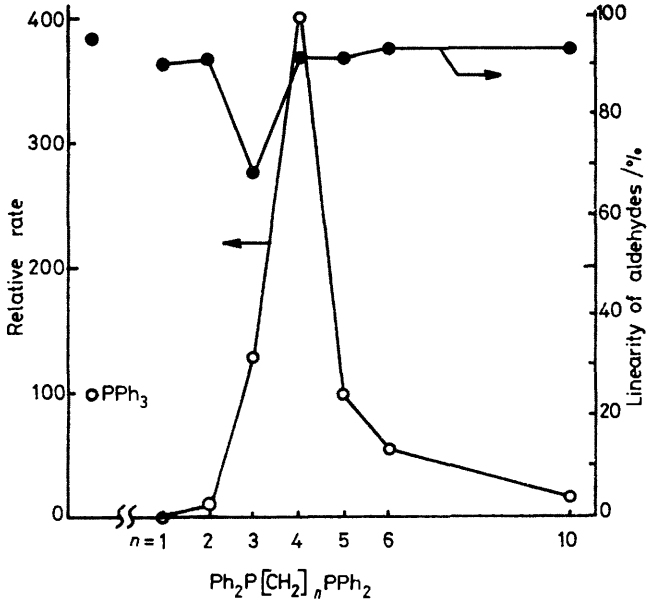


FIGURE 1. Hydroformylation of pent-1-ene. See Table for experimental conditions. Quantity of Pt complex used was $3{\cdot}2 \times 10^{-5}$ mol.

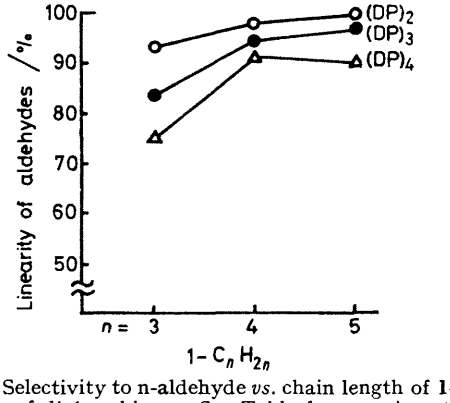


FIGURE 2. Selectivity to n-aldehyde *vs.* chain length of 1-olefins and ring size of diphosphines. See Table for experimental conditions.

TABLE. Hydroformylation of pent-1-ene by the use of platinum complex catalysts.[a]

| Run | Catalyst[b] | Temp. /°C | Time /h | Conversion/% | Relative rate[c] | Yield/% Aldehyde (n/iso) | n-Pentane | Pent-2-ene | Polymer |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $PtCl_2$–$2PPh_3$ | 100 | 24 | 3·8 | 1·0 | 3·0 (92/8) | 0·3 | 0·5 | 0·0 |
| 2 | $PtCl_2$–$Ph_2P[CH_2]_4PPh_2$ | 100 | 18 | 100 | 7·5 | 71·1 (91/9) | 13·9 | 15·0 | 0·0 |
| 3 | $PtCl_2$–$(DP)_4$ | 100 | 18 | 100 | 6·0 | 75·9 (90/10) | 13·3 | 10·4 | 0·4 |
| 4 | $PtCl_2$–$(DP)_3$ | 100 | 5 | 100 | 20·0 | 74·0 (97/3) | 8·8 | 14·3 | 2·9 |
| 5 | $PtCl_2$–$(DP)_3$[d] | 100 | 4 | 99 | 21·0 | 87·7 (96/4) | 2·9 | 8·4 | 0·0 |
| 6 | $PtCl_2$–$(DP)_2$ | 100 | 3 | 100 | 31·0 | 79·0 (99/1) | 6·4 | 13·4 | 0·2 |
| 7 | $HRh(CO)(PPh_3)_3$ | 100 | 4 | 100 | 23·5 | 100·0 (54/46) | 0·0 | 0·0 | 0·0 |
| 8 | $PtCl_2$–$(DP)_2$ | 70 | 2 | 100 | 40·0 | 88·6 (99/1) | 3·5 | 7·6 | 0·3 |
| 9 | $HRh(CO)(PPh_3)_3$ | 70 | 5 | 100 | 12·0 | 98·9 (70/30) | 0·0 | 1·1 | 0·0 |

[a] Carried out in a 50 ml stainless steel autoclave (SUS-316): pent-1-ene, 3 ml; benzene, 18 ml; $Pt(PhCN)_2Cl_2$, $3{\cdot}2 \times 10^{-6}$ mol for runs 1–7 and $3{\cdot}2 \times 10^{-5}$ mol for runs 8 and 9. Pt:P:Sn (atomic ratio) = 1:2:5. Initial pressure, 100 atm ($CO/H_2$ = 1) at 20 °C except run 5. [b] (DP): $Ph_2PCH_2\overline{CHCHX}CH_2PPh_2$ (*trans*); $(DP)_4$, X = $-[CH_2]_4-$; $(DP)_3$, X = $-[OCMe_2O]-$; $(DP)_2$, X = $-[CH_2]_2-$. [c] The maximum rate of pressure drop in run 1 was taken as the unit rate. [d] Initial pressure, 200 atm ($CO/H_2$ = 3) at 20 °C.

† Work is still in progress on the optimization of conditions.

Figure 2 shows that the linearity of the resulting aldehydes increased with an increase in the chain length of the 1-olefin and with a reduction in the ring size of the diphosphine. In the industrially useful hydroformylation of propene where positional isomerization is immaterial, the final yield of n-butanal from propene is much higher than that obtained with a Rh catalyst under our reaction conditions. A loose *cis*-co-ordination of the diphosphine which can barely form a strained and rigid seven-membered chelate ring would easily provide a vacant site for the activation of the reactants.

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[1] C. Hsu and M. Orchin, *J. Amer. Chem. Soc.*, 1975, **97**, 3553.
[2] I. Schwager and J. F. Knifton, *J. Catalysis*, 1976, **45**, 256.
[3] An exceptionally low selectivity at $n = 3$ was also observed in a Rh–diphosphine-catalysed α-hydroformylation of some αβ-unsaturated esters (M. Tanaka, T. Hayashi, and I. Ogata, *Bull. Chem. Soc. Japan*, 1977, **50**, 2351).