Phosphine *vs.* Phosphine Oxide Ligands in Hydroformylation Reactions

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In the hydroformylation of styrene catalysed by rhodium complexes, mixed amino phosphine oxide ligands show high reactivity and selectivity for the formation of the branched aldehyde.

The catalytic properties of low-valent transition metal complexes with bidentate phosphine ligands have been studied for many years.[1] Unfortunately most of these complexes, and in particular mononuclear compounds, require drastic pressure and temperature conditions when applied to hydroformylation.[2] Catalysts with mixed bidentate ligands (P–N, P–O, P–S) have received, so far, only limited attention and only a few studies on the utilization of complexes with such ligands in hydroformylation reactions have been reported.[3] Few cases have been reported in which complexes having biphosphine monoxide ligands (*e.g.* **1**) were found to be a better catalysts than the complexes having biphosphine ligands for the carbonylation of methanol.[4]

Recently we were engaged in preparing mixed bidentate ligands having phosphorus and nitrogen (*e.g.* **2**). These mixed bidentate ligands were found to lead to significantly improve catalysts for hydroformylation reactions of oelfins. To our surprise, phosphine oxide derivative **3** was found to form a more active catalyst than the tertiary phosphine analogue **2a** (n = 1, R = Me, R′ = Ph). These results contradict the well-known fact that phosphine oxides are often poor ligands for carbonylation catalysts.[5]

$$\mathrm{PhCH{=}CH_2 + CO{-}H_2 \xrightarrow[\text{CHCl}_3,\ 80\ ^\circ\text{C},\ 600\ \text{psi}]{[\{RhCl(cod)\}_2]\ +\ 3} PhCH(Me)CHO + PhCH_2CH_2CHO} \quad (1)$$

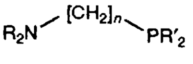
The reaction of styrene in chloroform under 600 psi of carbon monoxide and hydrogen (1 : 1) and a catalytic amount of $[\mathrm{RhCl(cod)}]_2$ **4** (cod = 1,5-cyclooctadiene) with **3** (170 : 1 : 2 ratio of styrene : **4** : **3**), at 80 °C for 1.5 h, resulted in 100% conversion to a 91 : 9 ratio of 2-phenylpropanal and 3-phenylpropanal [eqn. (1)].† The regiospecificity found here (Table 1) compares favourably with that in reports by others.[6] While styrene gave a good selectivity and conversion, dec-1-ene gave good conversion (100% under the conditions of Table 1) but poor selectivity (62% of the branched aldehyde) and α-methylstyrene gave low conversion (10%) with very high selectivity (100% of linear aldehyde). At higher pressure (1000 psi) α-methylstyrene gave 49% of the linear aldehyde.

Table 1 indicates that the catalytic system having ligand **3** is much better than the phosphine analogue **2a** for hydroformylation of styrene. While **3** gave 100% conversion in 1.5 h (or 80% in 1 h), **2a** gave only 59%. The pyridine ligand analogues of **3** and **2a** (*i.e.* **5** and **6**) gave moderate yields but there was no difference between the phosphine **5** and the phosphine oxide ligand **6**. We assume that the difference in activity between **3** and **6** is associated with the basicity of the amino and pyridyl groups. The amino group is of course more basic than the pyridine derivative. This property plays an important role in the stability of low-valent metal intermediates in catalysis.[7]

1

n = 1,2

3



2

n = 1,2,3
R′ = alkyl or aryl
R_2N = alkylamine or 2-pyridyl

$[\{\mathrm{RhCl(cod)}\}_2]$

4

It seems that these ligands are acting as chelating ligands,‡ forming various metallocycles with the rhodium atom under the hydroformylation conditions (see *e.g.* structures **11–13**). Replacement of ligand **3** by the quaternary ammonium ions $[\mathrm{Ph_2P(O)CH_2NMe_3}]^+\mathrm{X}^-$ (X = Cl, Br, I),§ as well as by $\mathrm{Ph_2P(O)Me}$, $\mathrm{PhC(O)CH_2NMe_2}$ or $[\mathrm{Ph_3PCH_2CH_2NMe_2}]^+\mathrm{Br}^-$ reduced the yield of the aldehydes to <10%.¶ Ligands **3**, **6**, **7** and **8** can form stable metallocycles of five and six membered rings, while **9** forms a less stable seven-membered ring. These properties of the ligands are in agreement with the results shown in Table 1. Although yields proved to depend on the nature of the ligands, the proportion of branched to linear aldehydes (87–92% branched) was found to be constant for all phosphine oxide ligands.

The hydroformylation reaction is sensitive to the Rh : ligand ratio, as one would expect from complexes having bidentate ligands.[8] The best $[\{\mathrm{RhCl(cod)}\}_2]$ to ligand ratio was found to be 1 : 2 (1 : 1 ligand : Rh atom); higher ratios of 1 : 4 or 1 : 8 decreased the yields (conversions of 81 and 69% respectively) but not the selectivity for formation of the branched aldehyde.

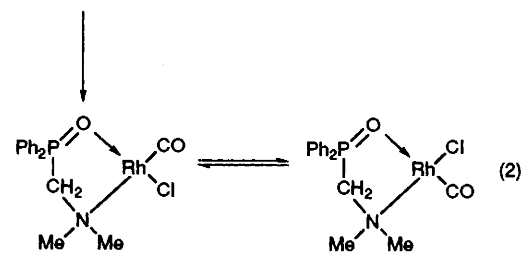
The catalytic system having **3** as a ligand was found to be very efficient when high styrene : **4** ratios were employed. Hydroformylation of styrene (**4** : substrate 1 : 1700) in chloroform and under 600 psi of CO and H_2 (1 : 1) for 5 h gave a 75% conversion and 90% selectivity for formation of the branched aldehyde. This catalytic system was found to be sensitive to the nature of the solvent. For example, under the conditions of Table 1, the use of tetrahydrofuran (THF) as solvent gave only 26% conversion to aldehydes (branched : linear, 86 : 14) and 4% of ethylbenzene (as hydrogenation product). Methylene chloride, 1,2-dichloroethane, carbon tetrachloride, toluene, pentane, acetone and ethanol gave 74, 30, 4, 7, 8, 5 and 5% conversion respectively, in the hydroformylation reaction. These results indicate that polar and non-coordinating sol-

Table 1 Hydroformylation of styrene catalysed by complex **4** and various mixed bidentate ligands[a]

Ligand	Conversion (%)	Aldehydes[b] Branched	Linear
—	7	95	5
$\mathrm{Ph_2PPy}$ **5**[c]	66	98	2
$\mathrm{Ph_2P(O)Py}$ **6**	61	92	8
$\mathrm{Ph_2PCH_2NMe_2}$ **2a**	59	94	6
$\mathrm{Ph_2P(O)CH_2NMe_2}$ **3**	100 (80)[d]	91	9
$\mathrm{Ph_2P(O)CH_2CH_2NMe_2}$ **7**	74	91	9
$\mathrm{Ph_2P(O)CH_2Py}$ **8**	63	87	13
$\mathrm{Ph_2P(O)CH_2CH_2Py}$ **9**	23	91	9

[a] Reaction conditions: see footnote †. [b] The aldehyde ratio was determined by GC and ^{1}H NMR. [c] Py = 2-pyridyl. [d] Conversion after 1 h.

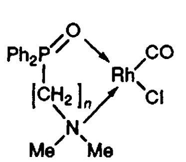
[{RhCl(CO)$_2$}$_2$] + 2Ph$_2$P(O)CH$_2$NMe$_2$



11a **11b** (2)

[{RhCl(CO)$_2$}$_2$]

10



11 $n = 1$
12 $n = 2$
13 $n = 3$

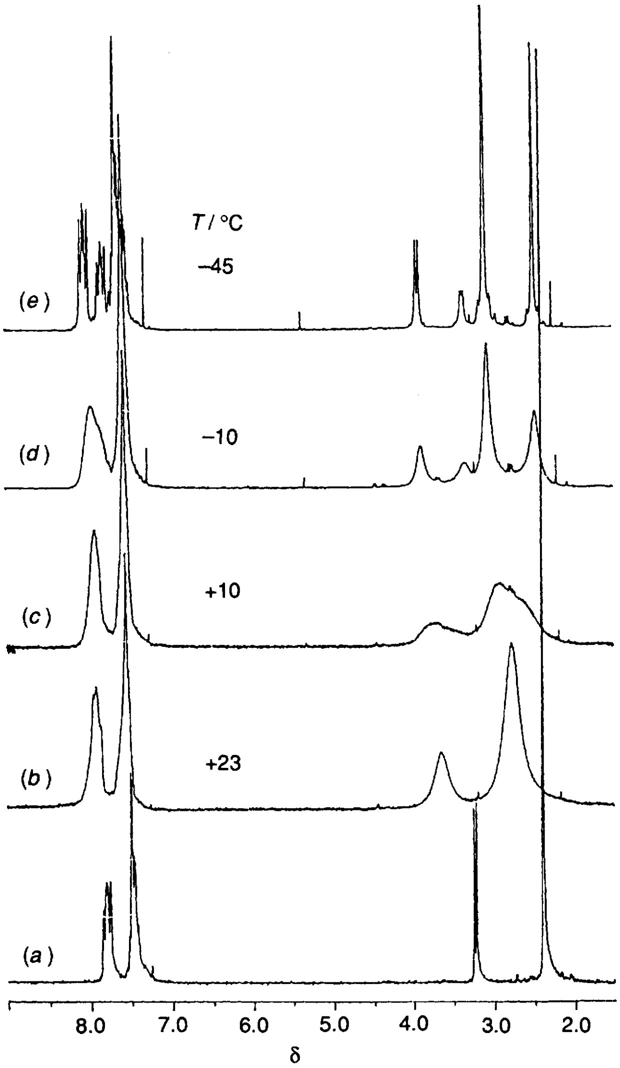


Fig. 1 ^{1}H NMR spectra of (*a*) ligand **3** and (*b–e*) complex **11** at various temperatures

vents are better than the coordinating solvents and the non-polar ones for hydroformylation of styrene using **3** as a ligand. Replacement of the rhodium precursor [{RhCl(cod)}$_2$] by the carbonyl complex [{RhCl(CO)$_2$}$_2$] **10** did not affect the hydroformylation of styrene. This thus indicates that [RhCl(CO)Ph$_2$P(O)CH$_2$NMe$_2$] **11** might be a catalyst precursor for the hydroformylation.

This assumption was supported by preparation of complex **11** *in situ* by addition of the rhodium complex [{RhCl(CO)$_2$}$_2$] to the ligand **3** in 1 : 2 ratio (**4** : **3**) in chloroform which led to the appearance of two CO IR absorptions (ν_{CO} 2084 and 2036 cm^{-1}) and a shift of the P=O stretching IR band of ligand **3** from 1265 to 1183 cm^{-1}. The 82 cm^{-1} shift in the IR spectrum indicates a significant weakening of the P=O bond and coordination of the phosphine oxide group to Rh. The phosphine oxide ^{31}P NMR signal is shifted 5.16 ppm downfield from the corresponding resonance of the non-coordinated ligand, indicative also of electron donation from the P=O group to Rh.||

The ^{1}H NMR spectrum of ligand **3** [Fig. 1(*a*)] is broadened and shifted downfield from that of the ligand on addition of **10** [Fig. 1(*b*)]. According to the equilibrium shown in eqn. (2), we expect the formation of two isomers of the complex **11**, and according to ^{1}H NMR data at different temperatures [Fig. 1(*b–e*)], it was found that below −45 °C the spectrum becomes sharp and gave two sets of peaks. This indicates the formation of two isomers [eqn. (2)]. Based on their ^{1}H NMR peaks they were present in 3 : 2 ratio at −45 °C.

Finally it is noteworthy that ligand **3** proved to be coordinated to the rhodium during the catalytic cycle, as a bidentate ligand in the beginning and the end of the catalytic cycle or monodentate coordinated through the nitrogen. Support for this assumption was provided by monitoring the structure of the rhodium complex with **3** in the catalytic reaction by ^{1}H and ^{31}P NMR and FTIR studies in the hydroformylation of styrene catalysed by **4** (styrene : Rh, 20 : 1), in which the ligand was coordinated to the metal during the catalytic cycle (0, 60, 100% conversion of styrene). In these three experiments using CDCl$_3$ as a solvent, the ^{1}H and ^{31}P NMR spectrum of the coordinated ligand **3** remained that of the complex **11**.|| These results indicate also that the reduction of the phosphine oxide to the phosphine under the conditions of the reaction is ruled out.

In conclusion, mixed amino phosphine oxide ligands display exceptionally high reactivity and regioselectivity in the hydroformylation of styrene to branched aldehyde as compared to the phosphine analogues. Catalysis by complexes with these ligands take place under mild conditions and requires only a simple work up.

This work was supported in part by the R. Bloch Research Center and the Ministry of Science and Technology through the Levi Eshkol Fund.

Received, 22nd June 1993; Com. 3/03599I

Footnotes

† *General procedure*: a mixture of styrene (2 mmol), [{RhCl(cod)}$_2$] (0.012 mmol) and ligand (0.024 mmol) in choloroform (2 ml) containing an internal standard (*p*-xylene; 2 mmol) was heated at 80 °C in an autoclave under CO–H$_2$ (600 psi; 1 : 1) for 1.5 h. The solvent was removed by rotary evaporation, and the residue was dissolved in ether and filtered through neutral alumina, which was then washed with additional solvent. The product mixture obtained by removal of the solvent was analysed by NMR spectroscopy and GC. products were identified by comparison of spectral data (^{1}H, ^{13}C NMR, IR, GCMS) with data for authentic samples.

‡ The high catalytic activity and regioselectivity of the Rh–**3** complex may be related to the reactivity of intermediate HRh(acyl)L (L = **3**). It seems that ligand **3** can accelerate the reductive elimination of aldehydes.[4]

¶ Other ligands such as 2,2′-bipyridine, *N,N,N′,N′*-tetramethylethylenediamine and piperidine gave only up to 5% conversion.

§ Addition of triethylamine to the quaternary ammonium ions gave a 6% yield of the aldehydes, indicating that the amino group did act as a coordinating group and not as a base.

‖ The ^{31}P NMR signals of the ligands **3**, **2a** and their rhodium complexes are: **3**, δ 27.684; **2a**, δ −25.34; **11**, δ 32.00; **2a**–Rh (analogue of **11**), δ +14.11 and +15.96.

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