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Phosphine oxides as ligands in the hydroformylation reaction

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Abstract

A new rhodium–phosphine oxide system has been investigated in the hydroformylation reaction. Some of the phosphine oxide ligands of type **2–12** (i.e. $R_2N(CH_2)_nP(O)R'_2$, R′ = Ph, Cy; n = 0, 1, 2, 3; R = Me, Et, ^{i}Pr, or NR_2 = 2-pyridyl) were found to be better ligands than the phosphine analogues (i.e. $R_2N(CH)_2PR'_2$) in the hydroformylation of olefins catalyzed by rhodium complexes. Detailed examination of factors controlling the selectivity for aldehydes formation revealed the following characteristics of the reaction: (a) use of ligands having bulkier amino groups decrease the yield of the aldehydes slightly; (b) ligands having amino groups with low basicity decrease the rate of the hydroformylation dramatically; (c) the electronic properties of the phosphine oxide group have no influence on the hydroformylation reaction; (d) uncoordinating solvents of low polarity such as dichloromethane, chloroform and toluene gave the best reaction rate and selectivity; (e) spectroscopic investigation of the hydroformylation of styrene catalyzed by rhodium with ligand **2** shows that the ligand is coordinated by the amino and the phosphine oxide groups under 1 atm of $CO-H_2$ and only by the amino group under 600 lbf in^{-2} of $CO-H_2$.

Keywords: Hydroformylation; Catalysis; Phosphine oxide; Aminophosphine; Rhodium

1. Introduction

Extensive studies on the structural features and catalytic properties of low valent transition metal complexes with mono and bidentate phosphine ligands have been reported [1]. Unfortunately, most of these complexes are not used in industrial processes because they require drastic conditions of pressure and temperature, when applied to hydroformylation. In addition, it is believed that oxidation of the triphenylphosphine ligands to the triphenylphosphine oxide (that are regarded as weak ligands) deactivates the catalyst [2]. It has, however, been shown that in some cases phosphine oxides not only do not interfere with the original catalyst but accelerate the insertion of carbon monoxide in a metal alkyl complex [3].

While we were investigating the structural and catalytic properties of rhodium complexes having mixed bidentate ligands (P–N, P–O) [4], we found that phosphine oxide analogues (i.e. P(O)–N, P(O)–O) are promoting ligands in the hydroformylation reactions catalyzed by rhodium complexes. To our knowledge there are previous reports in the literature using phosphine oxide as ligands in carbonylation reactions. In one case it has been reported that rhodium complexes having biphosphine monoxide as ligands (e.g. $Ph_2P(O)CH_2$-PPh_2) are active in carbonylation of methanol and were found to be better catalysts than the biphosphine analogues [5]. There are also a few reports in the literature using a mixture of phosphine–phosphine oxide as ligands in hydroformylations [6].

2. Results and discussion

The reaction of styrene in chloroform with a 1:1 mixture of carbon monoxide and hydrogen in the presence of catalytic amounts of $Rh_2Cl_2(Cod)_2$ and free $Ph_2P(O)CH_2NMe_2$ (**2**), (340:1:2 ratio of styrene [Rh]:**2**), at 80°C and 600 lbf in^{-2} for 1.5 h, results in a 100% conversion to a 91:9 ratio of 2-phenylpropanal

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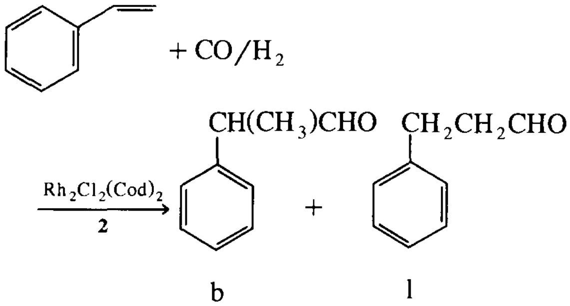
3-phenylpropanal (Eq. (1)). Only 5% hydroformylation reaction occurs in the absence of the amino phosphine oxide ligand [7].



(1)

This result is superior to those obtained in similar catalysts using the non-oxidized phosphine analogue of 2 (i.e. $Ph_2PCH_2NMe_2$) [4] and other non-conventional rhodium complexes [8]. The above conditions for the hydroformylation system were those obtained by detailed examination of the influence of different parameters on the rate and selectivity of the reaction. These factors are discussed below.

2.1. *Effect of the solvent*

The nature of the solvent is critical to the success of the hydroformylation reactions. Table 1 indicates the influence of the solvent on the conversion and selectivity in the hydroformylation of styrene. Solvents such as THF, 1,4-dioxane and acetone with medium rated polarity and coordinating properties gave low to medium conversions to aldehydes and have little effect on the branched/linear ratio. Neither very polar protic solvents (e.g. methanol) nor non-polar solvents (e.g. carbon tetrachloride, *n*-decane and *n*-pentane) led to appreciable conversions of olefin to aldehydes. Only non-coordinating low polar solvent such as CH_2Cl_2, $CHCl_3$ and toluene gave high conversions to aldehydes with very high branched/linear ratio (c.f. the same behavior observed in some other hydroformylation systems [9]).

2.2. *Electronic and steric effects of the substrate*

Table 2 indicates that 2-vinylnaphthalene like styrene gave good conversions and selectivity. The presence of a methyl group on the olefinic carbon atom bearing the aryl unit has a profound influence on the product distribution (Table 2). Both aromatic (e.g. α-methylstyrene) and aliphatic substrates (e.g. R-(+)-limonene) of 1,1-disubstituted olefins undergo hydroformylation affording the linear aldehyde as the only product. While 1,1-disubstituted olefins gave only one hydroformylation product, 1,2-disubstituted olefins (e.g. indene) gave a mixture of products with only low selectivity of preferential formation of the formyl group in the benzylic position. Monosubstituted double bonds react faster than disubstituted ones and the later react faster than trisubstituted olefins. Thus, R-(+)-limonene underwent hydroformylation only on the less substituted double bond.

The Rh–2 catalyst system is not very useful for hydroformylation of simple-monosubstituted olefins such as 1-decene, since the branched/linear aldehyde ratio is near unity.

Inhibition of the hydroformylation reaction by coordinating solvents (compared for example with chloroform) led us to explore the hydroformylation of vinyl ethers, with the idea that the oxygen atom bearing the double bond will coordinate to the rhodium metal and consequently lead to regioselectively formation of a product with the formyl group in the α-position to the oxygen atom (Eq. (2)). Indeed, vinyl ethers (e.g. phenyl vinyl ether) do undergo hydroformylation affording the branched chain product in quite high regioselectivity (Table 2).

2.3. *Effect of the temperature*

The temperature has a remarkable effect on the rate and the selectivity of the reaction. Table 3 indicates that in chloroform, the rate of hydroformylation increases with an increase in the temperature, but the selectivity decreases substantially. Optimal results were obtained at 80°C and therefore this was chosen as the standard temperature in most of our experiments. The reaction can be performed at room temperature in excellent selectivity but the rate is too slow.

2.4. *Effect of the hydrogen and carbon monoxide*

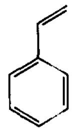
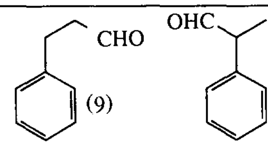
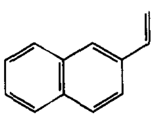
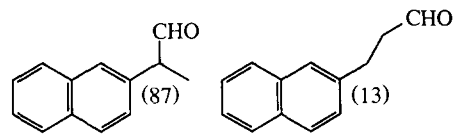
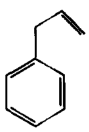
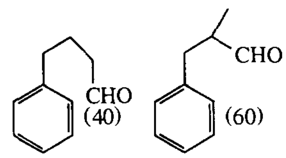
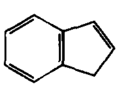
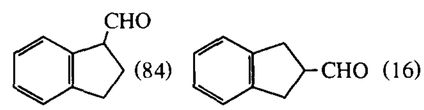
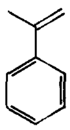
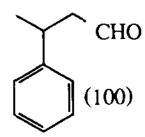
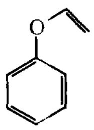
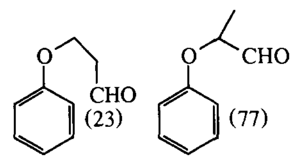
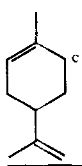
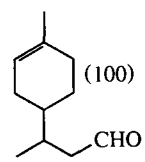
An increase in the total pressure of $CO:H_2$ (ratio 1:1) causes the rate to increase as well. It also leads to a small increase in the regioselectivity of the reaction (Table 4). Also, the ratio of $CO:H_2$ has in the case of styrene hydroformylation a remarkable effect on the rate and selectivity (Table 4). As the relative amount of CO

Table 1
Hydroformylation of styrene in various solvents [a]

Solvent	Yield (%)	Selectivity (b:l)
THF [b]	26	86:14
1,4-Dioxane	50	88:12
Acetone	5	92:8
n-Decane	22	86:14
n-Pentane	8	92:8
CCl_4	4	83:17
$ClCH_2H_2Cl$	30	89:11
CH_2Cl_2	74	88:12
C_2H_5OH	5	—
$CHCl_3$	100	91:9
Toluene	77	99:1

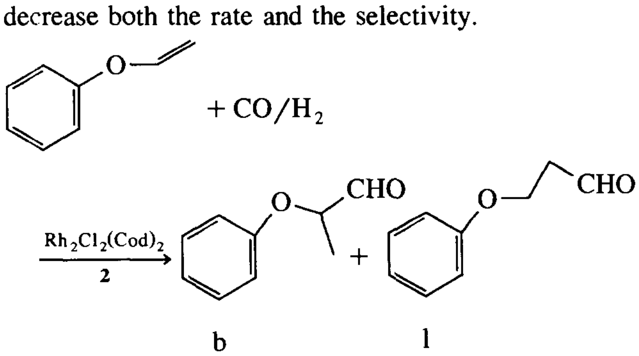
[a] Reaction conditions: 1 mmol styrene, 0.006 mmol $Rh_2Cl_2(Cod)_2$, 0.012 mmol ligand 2, 600 lbf in^{-2} $CO:H_2$ (1:1), 80±2°C, 1.5 h, 2 ml solvent. [b] 4% of ethylbenzene was formed.

Table 2
Hydroformylation of olefins catalyzed by rhodium and ligand **2** [a]

	Conversion (%)	Product (yield, %)
	100	 (9) (91)
= [b]	95	(10) (90)
	91	 (87) (13)
$CH_3(CH_2)_7CH=CH_2$	100	$CH_3(CH_2)_9CHO$ (62) $CH_3(CH_2)_7CH(CHO)CH_3$ (38)
	100	 (40) (60)
	34	 (84) (16)
 [c]	49	 (100)
	100	 (23) (77)
 [c]	83	 (100)

[a] Reaction conditions: 2 mmol substrate, 2 ml $CHCl_3$, 0.006 mmol $Rh_2Cl_2(Cod)_2$, 0.012 mmol **2**, 80°C, 600 lbf in^{-2} CO:H_2 (1:1), 1.5 h. [b] Styrene/Rh = 2500 for 25 h at room temperature. [c] 25 h.

increases, both the rate and selectivity of the reaction increases. However, higher CO:H_2 ratios than 1/1 decrease both the rate and the selectivity.



(2)

2.5. *The catalyst : substrate ratio*

As **2** is a weak coordinating ligand, we investigated the stability and efficiency of this new catalytic system. Table 5 indicates that in the case of styrene the system $Rh_2Cl_2(Cod)_2$–**2** is both stable and efficient. A styrene:Rh ratio of up to 10000 could be employed. The selectivity of the hydroformylation reaction decreases as the substrate:Rh ratio increases; this may be rationalized by the change in polarity of the medium that take place in the case of such a high ratio. It is possible to increase the selectivity in this case by lowering the temperature to 50°C.

We found that styrene hydroformylation by the $Rh_2Cl_2(Cod)_2$–**2** system can be carried out in a prepara-

Table 3
Influence of the temperature on the hydroformylation of styrene [a]

Temperature (±2°C)	Yield (%)	Selectivity (b:l)
25 [b]	20	99:1
45	3	99:1
65	53	95:5
80	80	92:8
90	98	81:19
115	100	53:47
25 [b]	20	99:1

[a] Reaction conditions: as in Table 2, 1 h. [b] 1000 lbf in^{-2}.

Table 5
Influence of styrene:Rh ratio on the hydroformylation reaction [a]

Ratio styrene:[Rh]	Time (h)	Yield (%)	Selectivity (b:l)
1700	5	81	87:13
1500 [b]	17	92	94:6
3350	16	100	83:17
5000	9	73	71:29
10000	15	81	71:29

[a] Reaction conditions: 0.006 mmol $Rh_2Cl_2(Cod)_2$, 0.012 mmol **2**, 2 ml $CHCl_3$, 80±2°C. [b] 50°C, 1000 lbf in^{-2}.

tive scale under the same conditions in a 3 l autoclave. The same results (98% yield of aldehydes) were obtained when a mixture of 100 mmol of styrene, 0.3 mmol of $Rh_2Cl_2(Cod)_2$, 0.6 mmol of **2** and 100 ml of $CHCl_3$ was shaken under 600 lbf in^{-2} of H_2 : CO (1 : 1) for 1.5 h at 80°C.

2.6. *The influence of the ligand structure*

The influence of the phosphine oxide ligand on the hydroformylation reaction is of particular interest. We prepared various mixed amino phosphine oxide ligands in order to determine the effect of the ligand structure on the rate and selectivity. Table 6 summarizes the results obtained with some representative phosphine oxides. The table indicates that the structure of the ligand has a substantial influence mainly on the yield, but only a small effect on the selectivity. Although changing the electronic properties of the P=O group by substitution of the phenyl groups in **2** by cyclohexyl groups (e.g. **3**) has no influence on the rate and selectivity of the reaction, and steric effects on the nitrogen have only a small effect on the yield of the reaction (e.g. **3**, **5**), electronic effects affect the rate significantly (e.g. **2**, **5**, **6**). Thus, replacing two of the methyl groups on the nitrogen in **2** by two phenyl groups (e.g. **6**) leads to a marked decrease in yield. We explain this decrease by the difference of basicity, which is a very important property in the case of weak ligands: the diphenyl amine derivative **6** is less basic than the dimethylamine in **2**. The importance of the ligand basicity is also noticed when the original amino group is substituted by a pyridyl moiety. Since the pyridyl group is less basic than the amino group, the pyridyl analogue of **2** (i.e. **10**) promoted the hydroformylation reaction less effectively. It should be mentioned that only 7% hydroformylation reaction occurs in the presence of amino ligands such as 2,2′-bipyridine, *N,N,N′,N′*-tetramethylethylenediamine, piperidine or triethylamine. The number of carbon atoms located between the amino and the phosphine oxide groups also plays an important role. An increase in the number of carbon atoms decreases the yield. We explain the reduction in yield by the difference in the stabilities of the metallacyclic intermediates **13**. While ligands **2** and **8** can form stable metallacycles of five and six membered rings, **9** and **12** form the less stable seven-membered ring. A similar observation was reported for rhodium and cobalt catalyzed hydroformylation reactions in the presence of diphosphine ligands

Table 4
The influence of the total pressure ($CO/H_2 = 1$) on the hydroformylation of styrene [a]

Pressure (lbf in^{-2})	CO/H_2	Yield (%)	Selectivity (b:l)
200	1	21	84:16
400	1	45	93:7
600	1	80	92:8
800	1	82	94:6
1000	1	88	95:5
1200	1	100	96:4
600	1/5	66	82:18
600	1/2	85	83:17
600	1/1	98	90:10
600	2/1	96	80:20
600	3/1	95	73:27
600	5/1	80	72:28

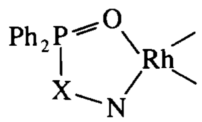
[a] Reaction conditions: as in Table 2.

Table 6
Hydroformylation of styrene catalyzed by rhodium and mixed phosphine oxide ligands [a]

Ligand	Yield (%)	Selectivity (b:l)
$Ph_2P(O)CH_2NMe_2$, **2**	100(80) [b]	91:9
$Cy_2P(O)CH_2NMe_2$, **3**	100(78) [b]	90:10
$Ph_2P(O)CH_2NEt_2$, **4**	96	87:13
$Ph_2P(O)CH_2N(i\text{-}pr)_2$, **5**	85	90:10
$Ph_2P(O)CH_2NPh_2$, **6**	25	97:3
$Cy_2P(O)CH(Ph)N(Me)_2$, **7**	100(74) [b]	91:9
$Ph_2P(O)CH_2CH_2NMe_2$, **8**	59	93:7
$Ph_2P(O)CH_2CH_2CH_2NMe_2$, **9**	75	94:6
$Ph_2P(O)Py$, **10**	61	92:8
$Ph_2P(O)CH_2Py$, **11**	63	87:3
$Ph_2P(O)CH_2CH_2Py$, **12**	63	97:3

[a] Reaction conditions: 2 mmol styrene, 2 ml $CHCl_3$, 0.006 mmol $Rh_2Cl_2(Cod)_2$, 0.012 mmol ligand, 600 lbf in^{-2} CO:H_2 (1:1), 80±2°C, 1.5 h. [b] 1 h.

[10], and in the case of carbonylation of methanol by Rh(I) and diphosphine monoxide ligand [5].



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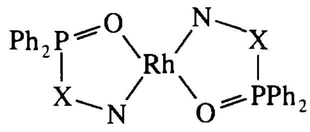
$X = (CH_2)_n$

N = dialkylamine or 2-pyridyl



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$X = (CH_2)_n$

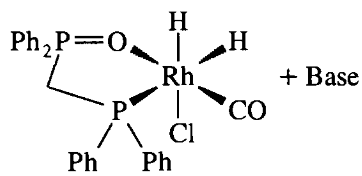
N = dialkylamine or 2-pyridyl

2.7. *Effect of the ligand: rhodium ratio*

The hydroformylation reaction was found to be sensitive to the ligand:Rh ratio. Table 7 shows that the preferred ligand:Rh atom ratio is 2. An increase in the ratio causes inhibition in the hydroformylation reaction owing to the formation of complexes of type **14** that are inefficient hydroformylation catalysts (see Ref. [1a]).

2.8. *Influence of some structural features of ligand 2*

Table 8 shows that structural changes in ligand **2** have a marked influence on the hydroformylation of styrene. Either substitution of the oxygen atom by sulfur or the phosphine oxide by a carbonyl group dramatically decreases the yield. The effect of a carbonyl group may be attributed to its electronic properties of the phosphine oxide [11]. Replacing the amino group by an alkoxy group (i.e. $Ph_2P(O)CH_2OCH_3$) is also associated with a decrease in catalytic activity. This decrease in activity is rationalized by the difference in basicity between the amino and alkoxy groups. Replacing the amino group in **2** by a more basic diphenylphosphino group (e.g. $Ph_2P(O)CH_2PPh_2$ (**1**)) inhibits the reaction owing to the stability of the intermediate Rh(III) dihydride complexes **15** (Eq. (3)) that is formed during the hydroformylation [12].



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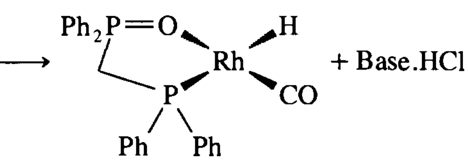

(3)

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This complex can be activated by the addition of an external base (e.g. the addition of Et_3N) which forms the reactive species $[(Ph_2P(O)CH_2PPh_2)Rh(CO)H]$ (**16**). Thus, addition of Et_3N to the reaction mixture of styrene, $Ph_2PCH_2P(O)Ph_2$ (**1**) and $Rh_2Cl_2(Cod)_2$ results in the production of a very effective catalytic hydroformylation system (Table 8). It seems that in the case of amino phosphine oxide ligands, unstable chlorine-containing rhodium hydride species are formed that rapidly lose HCl via a reductive elimination process. Replacement of the amino group in **2** by an ammonium group or phosphine oxide ligand cause a reduction in yield. Addition of an external base to this system did not improve the yield. This indicates that the amino group is not acting as a base in the hydroformylation. In order to prove that the ligand **2** is not acting as a monodentate ligand and that the amino group is not acting as a base in the hydroformylation reaction, we

Table 7
Influence of the ligand:Rh ratio on the hydroformylation of styrene [a]

Ligand	Yield (%)		
	Rh:**2** = 1:2	1:4	1:8
$Ph_2P(O)CH_2N(CH_2)_3$	100	81	69
$Ph_2P(O)CH_2CH_2N(CH_2)_3$	74	13	10
$Ph_2P(O)Py$	61	50	10
$Ph_2P(O)CH_2Py$	63	21	3
$Ph_2P(O)CH_2CH_2Py$	23	18	—

[a] Reaction conditions: 2 mmol styrene, 2 ml $CHCl_3$, 0.006 mmol $Rh_2Cl_2(Cod)_2$, 600 lbf in^{-2} $CO:H_2$ (1:1), 80 ± 2°C, 1.5 h.

Table 8
Hydroformylation of styrene catalyzed by rhodium and various ligands

Ligand	Yield (%)	Selectivity (b:l)
$Ph_2PCH_2NMe_2$	59	94:6
$Ph_2P(O)CH_2NMe_2$	100	92:8
$Ph_2P(S)CH_2NMe_2$	0	—
$PhC(O)CH_2NMe_2$	12	87:13
$CH_3C(O)CH_2NMe_2$	20	85:15
$Ph_2P(O)CH_2OMe$	5	90:10
$[Ph_2P(O)CH_2NMe_3]^+ X^-$ X = Cl,Br,I	5	—
$[Ph_3PCH_2NMe_2]^+ Br^-$	5	90:10
$Ph_3P(O)CH_3 + NEt_3$ [b]	5	—
$Ph_2P(O)CH_2PPh_2$	6	94:6
$Ph_2P(O)CH_2PPh_2$ [c]	95	93:7
$Ph_2P(O)CH_2P(O)Ph_2$ [d]	0	—

[a] Reaction conditions: as in Table 2. [b] 0.048 mmol ligand and 0.048 mmol amine. [c] 0.024 mmol triethylamine was added. [d] 2 h.

Table 9
Hydroformylation of styrene catalyzed by ligand **2** and different complexes [a]

Ligand	Time (h)	Yield (%)	Selectivity (%b)
$Rh_2Cl_2(Cod)_2$	1.5	100	92
$[Rh(O_2CC_7H_{15})_2]_2$	1.5	72	84
$Rh_2Cl_2(CO)_4$	1.5	95	87
$(Ph_3P)_3RhCl$	8	0	—
$Ir_2Cl_2(Cod)_2$ [b]	3	15	98
$RhCl_3 \cdot 3H_2O$	5	—	—
$Rh_6(CO)_{16}$ [c]	3	90	87
$Co_2(CO)_8$	3	—	—

[a] Reaction conditions: 0.006 mmol catalyst, 0.012 mmol **2**, 2 mmol styrene, 80 ± 2°C, 600 lbf in^{-2} CO:H_2 (1:1), 2 ml $CHCl_3$. [b] 10% hydrogenation. [c] **2**/Rh = 3.

replaced **2** by methyldiphenylphosphine oxide and triethylamine. The yield of hydroformylation of styrene by this catalyst system remained very low. This shows clearly that such ligands are active as a bidentate in the reaction.

2.9. Activity of various metal precursors

Table 9 shows the results of the hydroformylation of styrene catalyzed by various metal complexes in the presence of **2**. The addition of ligand **2** has a crucial influence on the reactivity of rhodium(I) complexes (e.g. $Rh_2Cl_2(Cod)_2$ and $[RhCl_2(CO)_2]_2$), but no influence on Wilkinson catalyst $(Ph_3P)_3RhCl$ [13]. Rhodium carboxylate complexes are less reactive than Rh(I) complexes and rhodium(III) (e.g. $RhCl_3 \cdot H_3O$) were inactive under the hydroformylation reaction. Iridium(I) complex (e.g. $Ir_2Cl_2(Cod)_2$) gave very low yield of aldehydes accompanied by the hydrogenation product (ethylbenzene).

Surprising is the stable rhodium carbonyl cluster $Rh_6(CO)_{16}$; this complex in the presence of **2** led to a particularly high rate of styrene hydroformylation products. We assume that the cluster dissociates to smaller clusters or even mono nuclearic species under the hydroformylation conditions [1c].

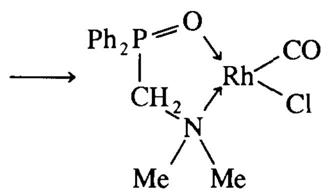
2.10. Mechanistic considerations

In order to understand the mechanism and the mode of coordination of the amino phosphine oxide ligands to the rhodium metal, we performed the following experiments

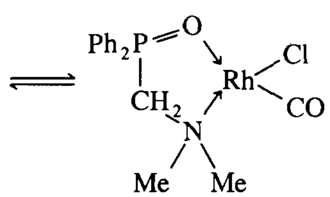
Initially we prepared in situ the rhodium chloro carbonyl complexes having amino phosphine oxide ligands (e.g. LRhCl(CO) **17**, L = amino phosphine oxide ligand) either by reacting the precursor $Rh_2Cl_2(Cod)_2$ followed by introduction of CO into the mixture for a few or by direct interacting of $[RhCl(CO)_2]_2$ with the ligand under argon. In the mixture complex, **17** (l = **2**) could be detected and characterized spectroscopically. Thus, in the case of ligand **2**, two CO absorption bands (ν_{co} = 2084 and 2036 cm^{-1}) appeared and a shift of the P=O stretching band from 1265 to 1183 cm^{-1} was detected. This shift in the IR spectrum indicates a significant weakening of the P=O bond and coordination of the phosphine oxide group to the Rh nucleus.

The ^1H NMR spectrum of ligand **2** is broadened and shifted downfield from that of the free ligand on addition of $Rh_2Cl_2(CO)_4$. Upon lowering the temperature to −45°C, the spectrum sharpened and revealed two sets of peaks. This indicates the formation of two isomers **17a** and **17b** (Eq. (4)).

$[RhCl(CO)_2]_2 + 2Ph_2P(O)CH_2NMe_2$



17a



(4)

17b

Based on their ^1H NMR peaks, the ratio between them was found to be 3:2 at −45°C [7].

In the case of ligand **10** ($Ph_2P(O)Py$), which is more rigid than ligand **2**, the shift in the ^{31}P NMR was larger than in the case of ligand **2** (Table 10); the peak at 21.53 ppm of the free ligand shifted to 33.90 ppm when $Rh_2Cl_2(CO)_4$ was added. The shift in the ^1H NMR and IR of the free and the complexed ligand shown in Table 10 also indicate a coordination of the ligand with the rhodium through the phosphine oxide and amino moieties.

It seems that **2** is coordinated to the rhodium during the catalytic cycle, either as a bidentate ligand, at least in the beginning and the end of the catalytic cycle, or as a monodentate coordinated through the nitrogen atom. Support in this assumption was provided by monitoring the structure of the rhodium complex with **2** in the catalytic reaction by ^1H and ^{31}P NMR and FTIR studies. Thus, hydroformylation of styrene catalyzed by $Rh_2Cl_2(CO)_4$ and ligand **2** (styrene:Rh = 20:1) shows that the ligand was coordinated to the metal during the catalytic cycle (at 0, 60, 100% conversion of styrene). In these experiments, using $CDCl_3$ as a solvent, the ^1H NMR and ^{31}P NMR spectrum of the coordinated ligand **2** remains that of complex **17**.

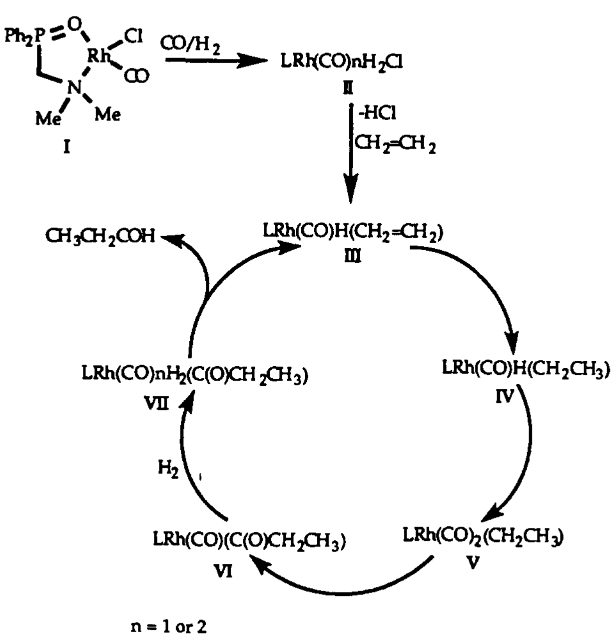
Table 10
Spectroscopic data of free mixed phosphine oxide ligands and their rhodium complexes

Ligand L	IR (cm^{-1})		NMR (ppm)	
	$\nu_{C=O}$	$\nu_{P=O}$	^1H	^{31}P
$Ph_2P(O)CH_2NMe_2$	—	1265	7.46–7.85 (m, 10H), 3.2(d, 2H), 2.38 (s, 3H)	27.7
$Ph_2P(O)CH_2NMe_2$ [a]	2084, 2036	1183		32.8
$Ph_2P(O)Py$	—	1182	8.78(d, 1H)8.31(t, 1H), 7.88(m, 4H), 7.49(m, 8H)	21.5
$Ph_2P(O)Py$ [a]	2088, 2034	1124	8.94(d, 1H), 8.05(m, 2H), 7.86(m, 4H), 7.57(m, 7H)	33.9
$Ph_2P(O)CH_2OMe$	—	1201	7.64(m, 4H), 7.38(m, 6H) 4.15(d, 2H), 3.32(s, 3H)	27.06
$Ph_2P(O)CH_2OMe$ [a]	2082, 2035,	1152	7.95(m, 4H), 7.27(m, 6H) 4.48(d, 2H), 3.16 (s, 3H)	45.94

[a] As LRhCl(CO) complex.

Running a hydroformylation reaction of styrene in $CDCl_3$ at 600 lb in^{-2} of $CO:H_2$ (1:1) by means of NMR measurements in a high pressure tube, shows no coordination between the rhodium metal and the phosphine oxide moiety in the ^{31}P NMR without any change of the ^{31}P NMR of the free ligand. This may indicate that the mixed phosphine oxide ligands are opened under pressure of CO to form a monodentate ligand. A similar behavior was observed when **2** was substituted by the diphosphine monoxide $Ph_2PCH_2P(O)Ph_2$ [5].

These experiments and other results suggest the mechanism outlined in Scheme 1, which resembles to traditional reported hydroformylation mechanism [14]. The ligand $Ph_2P(O)CH_2NMe_2$ in intermediate **II** is probably a monodentate ligand under pressure of CO.



Scheme 1.

This intermediate seems to be unstable in the case of **2** and other amine phosphine oxide ligand, and loses HCl easily to form **III** in the presence of olefin, while in the case of diphosphine monoxide ($Ph_2PCH_2P(O)Ph_2$) intermediate **II** seems neither to lose HCl nor be converted to **III**. This is due to the difference in the pK_a of the hydride complex that depends partly on the nature of the coordinated ligands [12]. The cluster $Rh_6(CO)_{16}$ and ligand ($Ph_2PCH_2P(O)Ph_2$) (ratio 1:3) forms a very active hydroformylation system that needs no addition of a base. It probably forms intermediate **III**. This supports the idea that complex $[(Ph_2P(O)CH_2PPh_2)RhH_2Cl(CO)]$, which is not formed in the case of $Rh_6(CO)_{16}$, is stable and does not catalyze the hydroformylation reaction. The mixed bidentate ligand may accelerate the insertion reactions **III** → **IV** and **V** → **VI** and the reductive elimination step **VII** → **III** shown in Scheme 1 [3,15].

In conclusion, it seems that mixed phosphine oxides are excellent ligands for the hydroformylation of olefins and compete successfully with the traditional mono and polyphosphine ligands. Their activity is superior, they are easily prepared and highly stable. These properties make them attractive for industrial application.

3. Experimental

Solvents were purified according to standard procedures. ^1H and ^{31}P NMR were performed on a Bruker WP-200SY spectrometer. IR spectra were recorded on a Nicolet 5ZDX FT-IR spectrometer. Mass spectra were obtained on a GC-MS spectrometer, with a mass selective detector HP 5971A and on a VG5050 micromass spectrometer.

The platinoid metal complexes were commercially available. Ph_2PH [16], $Ph_2P(S)CH_2NMe_2$ [17],

$Ph_2P(O)CH_2CH_2NMe_2$ [18], $Ph_2P(O)CH_2CH_2NMe_2$ [18a], $Ph_2P(O)(CH_2)_3NMe_2$ [18a,b], $[Ph_2P(O)CH_2NMe_3]^+I^-$ [18c], $Ph_2P(O)CH_2PPh_2$ [19,20], $Ph_2P(O)CH_2Py$ [21], $Ph_2P(O)Py$ [22], $Ph_2P(O)CH_2Py$ [23], $Ph_2P(O)CH_2OMe$ [24] were prepared by literature procedures by oxidation of the corresponding phosphines.

Ligands of the general formula $R_2P(O)CH_2NR'_2$ (R = Ph, Cy; R′ = Me, Et, ^iPr, Ph) were prepared by modification of the literature procedures [25–27] Compounds **2** and **3** (R = Ph, Cy; R′ = Me) were preparation as follows:

(i) $[Me_2N=CH_2]^+Cl^-$, 0.27 mol, THF, 35 ml and 0.03 mol K_2CO_3 were stirred in a three-necked flask (50 ml) under argon. After cooling the reaction mixture to 0°C a mixture of 10 ml THF and 0.027 mol of R_2PH was added during 30 min. The mixture was stirred for another 2 h. Concentration of the reaction mixture under reduced pressure, addition of ether (40 ml) and water (20 ml), extraction, drying of the organic phase and evaporation of the solvent led to the formation of a colorless liquid in 70–75% yield (phosphine analogues of **2** or **3**) after distillation.

(ii) $R_2PCH_2NR'_2$, 0.02 mol and 30 ml of acetone were added to a three-necked flask. The mixture was cooled to 0°C and 6.8 g of 10% H_2O_2 in 10 ml of acetone was added during 30 min. The mixture was then refluxed for 1 h. Cooling and evaporation of the solvents gave to a white suspension. Extraction with *n*-hexane and evaporation of the solvent furnished white solids (**2** or **3**) in 90% yield.

3.1. General procedure for the hydroformylation reaction

A mixture of 2 mmol of styrene, and 0.012 mmol of $[RhCl(Cod)]_2$ and 0.024 mmol ligand in chloroform (2 ml) containing 2 mmol of an internal standard (*p*-xylene) was heated for 1.5 h at 80°C in an autoclave using a 1 : 1 $CO:H_2$ mixture (see Table 1). The solvent was removed with the aid of rotary evaporation, and the residue dissolved in ether and filtered through neutral alumina. The mixture of products that was obtained after removal of the solvent was subjected to NMR and GC analysis. Products were identified by comparison of their spectral data (^1H, ^{13}C NMR, IR, GCMS) with those authentic samples.

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