ELSEVIER

Coordination Chemistry Reviews
190–192 (1999) 883–900

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Perspectives of rhodium organometallic catalysis. Fundamental and applied aspects of hydroformylation

Anna M. Trzeciak, Józef J. Ziółkowski *

Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland

Accepted 6 April 1999

Contents

Abbreviations: BINAS, sulfonated 2,2′-bis(diphenylphosphinomethyl)-1,1′-binaphtyl; BISBI, 2,2′-bis-(diphenylphosphinomethyl)-1,1′-biphenyl; cod, cyclooctadiene; L, ligand; LPO, low pressure oxo; M, transition metal; PC, diphenylphosphinomethyl-2-succinate, dilithium salt, $Ph_2PCH_2CH(CO_2Li)(CH_2CO_2Li)$; PH, diphenylphosphino-methacrylic acid, $Ph_2PCH_2CH(CH_3)(CO_2H)$; PNa, diphenylphosphino-methacrylate, sodium salt, $Ph_2PCH_2CH(CH_3)(CO_2Na)$; PNS, *N*-[1′,1′-dimethyl-2,-ethanesulfonate]diphenylphosphine-3-propanamide, lithium salt, $Ph_2PCH_2CH_2(CO)NHC(CH_3)_2CH_2SO_3Li$; UCC, Union Carbide Company; TPPTS, tri-(3-sulfophenyl)-phosphine, sodium salt, $P(C_6H_4\text{-}3\text{-}SO_3Na)_3$; TPPDS, di-(3-sulfophenyl)-phenylphosphine, sodium salt, $PPh(C_6H_4\text{-}3\text{-}SO_3Na)_2$; TPPMS, diphenyl-(3-sulfophenyl)-phosphine, sodium salt, $PPh_2(C_6H_4\text{-}3\text{-}SO_3Na)$; XANTPHOS, 9,9-dimethyl-4,6-bis(diphenylphosphino)xanthene; NAPHOS, 2,2′-bis(diphenylphosphinomethyl)-1,1′-binaphtyl.

* Corresponding author. Tel.: +48-71-3204257; fax: +48-71-3282348.
E-mail address: jjz@wchuwr.chem.uni.wroc.pl (J.J. Ziółkowski)

PII: S0010-8545(99)00127-7

Abstract

Today's hydroformylation process almost exclusively use rhodium homogeneous catalysts. Some domination of octacarbonyl dicobalt as the catalyst precursor was followed with broad application of rhodium based organometallic catalysts modified with mainly phosphorus ligands of different donor–acceptor properties and/or different cone/bite angles. Although there are many papers dealing with the comparative studies on structure-reactivity correlation, the effects of electronic and steric parameters of P-ligands on the catalytic activity of rhodium catalysts are not always predictable. Phosphines and phosphites as ligands, simple and structurally developed, bulky, mono and bidentate are still of great interest in the modification procedures of rhodium catalysts, especially when high regioselectivity in the hydroformylation is expected. Further development of the synthesis of phosphorus ligands led to the preparation of water soluble ligands and the creation of a new class of two-phase homogeneous catalysts, in this way solving problems of separation and/or catalysts reuse. Some new water soluble phosphines (PNS, PNa, PC) as well as *N*-pyrrolyl phosphines ($PPh_x(NC_4H_4)_{3-x}$) of required electronic parameters applied for synthesis of new rhodium catalyst precursors will be discussed and the results of structural studies will be used in the explanation of the observed catalytic activity in the model hydroformylation reaction of olefins (1-hexene, unsaturated alcohols) as well as related reactions, i.e. isomerization and hydrogenation.

Keywords: Hydroformylation; Phosphorus modifying ligands; Rhodium catalysts; Water soluble catalysts; Bimetallic catalytic systems

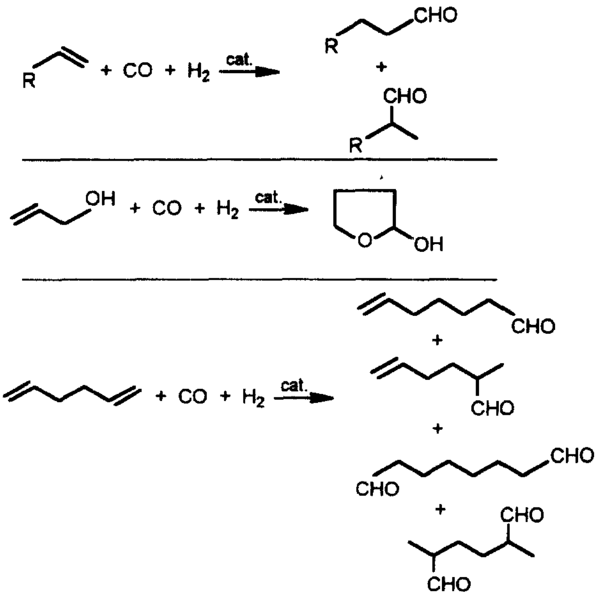
1. Introduction to hydroformylation reaction

Catalytic hydroformylation reactions are mainly applied for aldehyde synthesis according to a nearly 60-year old process, discovered in 1938 by Otto Roelen in Germany [1] (Scheme 1).

Aldehydes are considered as industrially important raw materials. Typical chemicals obtainable from aldehydes are shown in Scheme 2.

Homogeneous catalysts based on dicobaltoctacarbonyl catalyst precursors, although still used, were replaced by many very active and selective new catalysts derived from rhodium organometallic compounds modified with different phosphorus ligands. Typical homogeneous catalysts in their reactive form are usually mono- or polynuclear hydrido-carbonyl complexes modified with donor–acceptor ligands L. Generally accepted orders of transition metals [M] activity and monodentate ligand [L] modifying ability are shown in Scheme 3 [2–5], however it is still not clear how phosphorus ligands control the selectivity of hydroformylation [6].

Very recent studies totally prove the classification above and demonstrate the significant advantage of rhodium based precursors and phosphorus modifying ligands in designing an active and selective hydroformylation catalyst. Other transition metals are much less attractive, however properly selected and designed modifying ligands may create unexpected catalytic activity of metals other than Co or Rh.



Scheme 1. Examples of the hydroformylation reactions.

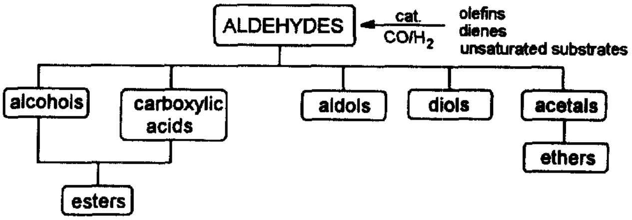
The future development of hydroformylation has both an economic and scientific aspect, the latter in respect to understanding the reaction mechanism.

2. Commercial applications

The commercial application of active and selective rhodium catalysts and increase of aldehyde production capacities are the factors seriously determining the intensity of research in the field of new catalyst design.

Some of the most important industrially implemented oxo process based on Co and Rh catalysts are shown in Table 1.

The following main conclusions can be drawn from the data presented in Table 1:



Scheme 2. Chemicals easy to obtain from aldehydes.

CATALYST PRECURSOR +[M]+MODIFYING LIGAND [L]

$$\downarrow \text{CO} \mid \text{H}_2$$

$$\mathrm{HM(CO)_xL_y} \quad \text{or} \quad \mathrm{H_xM_y(CO)_zL_n}$$

$$\mathrm{M = Rh >> Co > Ir,\ Ru > Os > Pt > Pd > Fe > Ni}$$

$$\mathrm{L = PPh_3,\ P(OR)_3 > P(n\text{-}C_4H_9)_3 >> NPh_3 > AsPh_3,\ SbPh_3 > BiPh_3}$$

Scheme 3. General composition of catalytic system for hydroformylation and orders of metal activity and ligand L modifying effect [2–5].

1. Rhodium based catalysts are more active and selective.
2. Non-modified catalysts are less selective (lower *n*/*iso* factor) and their industrial application requires more energy consumption.
3. Water soluble systems are promising as very selective (high *n*/*iso*) and environmentally friendly.

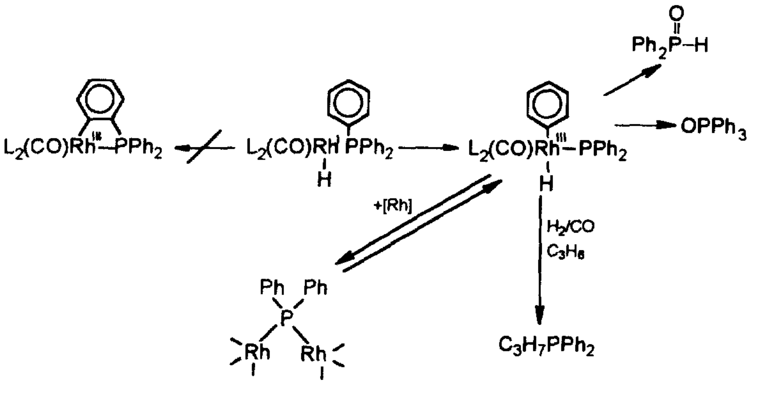
LPO (low pressure oxo) process (Union Carbide) [7] which in the first version introduced the so called 'gas recycle' allowing removal of the C_4 aldehydes formed from propene hydroformylation with the rate of its formation, was replaced in the latest UCC process by the so called 'liquid recycle'. The advantage of the latest UCC process is not only the much longer lifetime of the rhodium catalyst used but also economically better parameters of the process. There are many spectacular examples showing the possibilities of the UCC process improvement by selection of proper phosphorus modifying ligands and application to the more selective and efficient catalyst preparation.

A variety of commercial processes has been developed and implemented owing to significant results in theoretical and experimental studies on catalyst structure–reactivity correlations, including very detailed investigations on the synthesis and

Table 1
Industrial oxo processes[a]

Company	Precursor and active form of catalyst	Modifying ligand L	T (°C) = p (bar)	*n*/*iso*
BASF, Rurhchemie	$Co_2(CO)_8$, $HCo(CO)_4$	None	150–180°C, 200–300 bar	2–4
Shell	$Co_2(CO)_8$, $HCo(CO)_3L$	Phosphines	160–200°C, 50–150 bar	7
Ruhrchemie	$Rh_4(CO)_{12}$, $HRh(CO)_4$	None	100–140°C, 200–300 bar	ca. 1
Union Carbide, Davy Powergass, Johnson–Matthey, LPO	$(acac)Rh(CO)_2$, $(acac)Rh(CO)PPh_3$, $HRh(CO)(PPh_3)_3$	PPh_3	60–120°C, 10–50 bar	ca. 11.5
Ruhrchemie, Rhone Poulenc	$[RhCl(1,3\text{-}cod)]_2$, $HRh(CO)(TPPTS)_3$	TPPTS	110–130°C, 40–60 bar	≥19

[a] See Ref. [5,7–11]



Scheme 4. Postulated mechanisms of catalyst degradation.

application of new modifying ligands as well as on the studies of deactivation of catalysts.

3. Rhodium organometallic catalysts deactivation and the role of orthometallation

The deactivation (life time) of homogeneous catalysts seems to be the most important factor limiting the practical application of the many extremely active but chemically unstable catalysts. Extended studies on deactivation of catalysts allowed one to design not only selective but also very stable homogeneous catalytic systems for hydroformylation.

Deactivation of the widely used rhodium catalysts, modified with monodentate triarylphosphines proceeds most probably via degradation of the phosphorus ligand which leads finally to a decrease in catalyst activity [12–14].

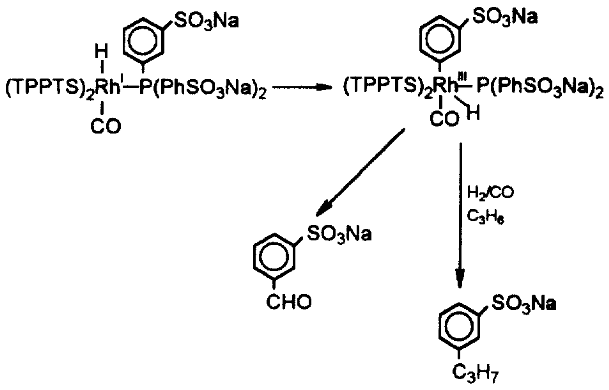
The formation of less active phosphido-bridged rhodium carbonyl organometallic species is generally used to explain the deactivation process [13–16].

Catalyst deactivation can also be initiated by the insertion of rhodium(I) into the carbon–phosphorus bond of PPh_3 followed by a two electron transfer from Rh(I) to the C–P bond (Scheme 4) [13–16]. All these processes leading to a decrease of the catalyst activity can be explained by several reactions:

1. the formation of a less active rhodium complex with $C_3H_7PPh_2$ phosphine or binuclear, bridged phosphido species $-Rh-PPh_2-Rh-$;
2. elimination of PPh_3 from the coordination sphere as $OP(H)Ph_2$ or $OPPh_3$.

A similar process may contribute to the deactivation of the water soluble rhodium–TPPTS catalyst (Scheme 5) [17,18].

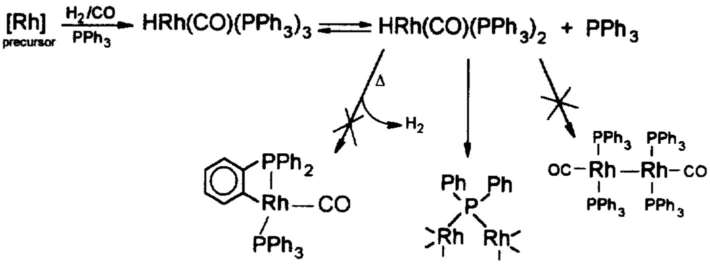
According to Ref. [15] deactivation of the $HRh(CO)(PPh_3)_3$ active form of the catalyst, observed at high temperature (> 100°C) is caused mainly by the formation of a phosphido-bridged dimeric rhodium complex. The formation of orthometallated or dimeric complexes with Rh–Rh bonds at these conditions are unlikely (Scheme 6), although they were found in other reactions [19,20].



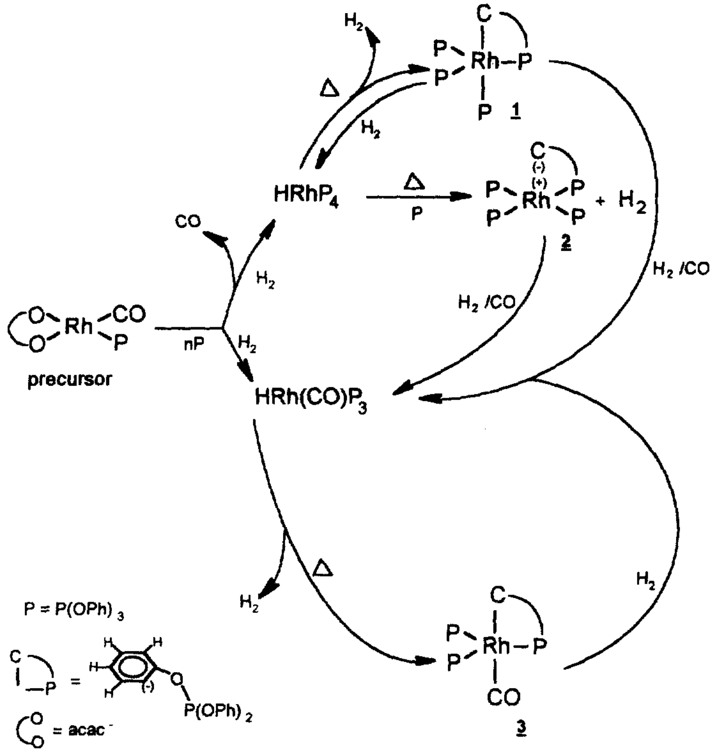
Scheme 5. Possible deactivation mechanism of water soluble rhodium–TPPTS modified catalyst.

A quite different situation may appear in the case of rhodium(I)–triphenylphosphite complexes used as catalyst precursors. Orthometallation in this case appears to be a rather stimulating step in hydroformylation and does not contribute to catalyst degradation (Scheme 7). As can be seen from Scheme 7 both catalytically active species, $HRh\{P(OPh)_3\}_4$ and $HRh(CO)\{P(OPh)_3\}_3$ are easily formed 'in situ' from corresponding orthometallated complexes. Orthometallated complexes 1, 3 and pseudo orthometallated complex 2, contrary to the orthometallated phosphino complex, are extremely reactive towards dihydrogen under very mild conditions. During the hydroformylation reaction they are totally converted into $HRh(CO)\{P(OPh)_3\}_3$ and only traces of the orthometallated species were detected in the reaction mixture.

These discrepancies suggest that there is still no general explanation for a degradation mechanism of the rhodium–phosphorus ligand modified catalytic system and therefore extended studies in this area are needed in the future.



Scheme 6. Alternative pathways of deactivation mechanism.

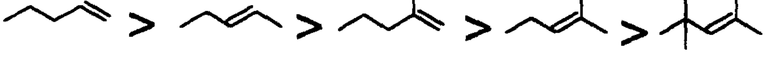


Scheme 7. Orthometallation (**1**) [21–23], (**3**) [24] and pseudo-orthometallation (**2**) [25–27] in rhodium(I)-triphenylphosphite modified catalysts as stimulating steps in catalytically active species formation.

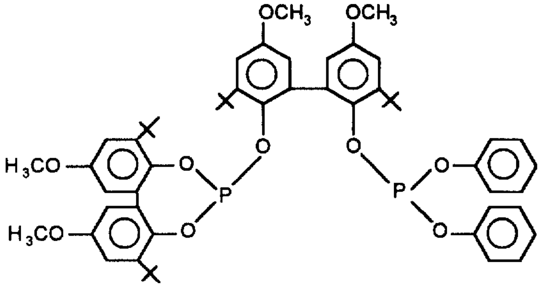
4. Phosphorus modifying ligands

The activity of rhodium based homogeneous catalysts modified with different phosphorus ligands depends strongly on the structure of the unsaturated substrates. Hydroformylation can be applied to a broad representation of unsaturated substrates containing simple carbon–carbon double bonds or some heteroatom–carbon double bonds. From a practical point of view unbranched terminal olefins such as propene, 1-butene, 1-octene etc. are the most important substrates and are usually more reactive than branched and internal olefins. The generally accepted order of reactivity of unsaturated substrates is presented in Scheme 8 [2–5].

However, the industrial importance of hydroformylation is not limited just to the rather simple olefins mentioned above. Hydroformylation may also be applied to



Scheme 8. The order of olefin reactivity in hydroformylation reactions.



Scheme 9. Bis-phosphite ligand [34,35].

many rather very complex unsaturated substrates with one or more functional groups.

Rhodium catalysts applied for hydroformylation of such substrates are usually modified with extraordinary ligands [28–33]. A good example of such processes is the hydroformylation of C_4 feedstock containing a mixture of butenes (Union Carbide and Davy Powergass Process Technology) in which the rhodium catalyst precursor is modified with a bulky bisphosphite ligand (Scheme 9) producing over 94% of *n*-pentanal [34,35].

The evolution of rhodium-based hydroformylation processes is illustrated well by the commercial applications of olefin hydroformylation in which different rhodium catalyst precursors modified with a broad variety of ligands, especially phosphorus ligands like phosphines and phosphites of different structure have been used [28–33].

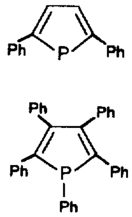
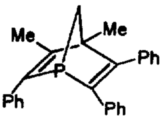
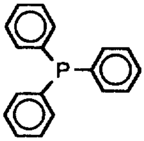
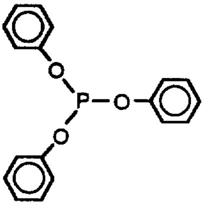
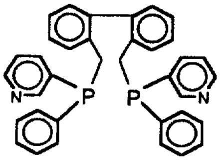
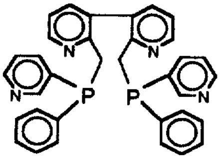
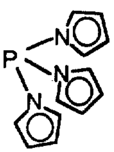
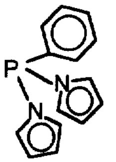
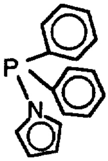
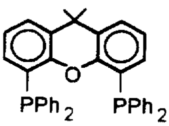
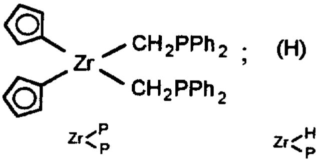
Recent progress in hydroformylation reactions has been caused mainly by the ligands synthetic methodology development. Designing new modifying phosphorus ligands has became an art, important for the creation of highly effective and selective new catalytic systems for hydroformylation. In Table 2 different examples of phosphorus mono- and bidentate ligands are collected in which the donor–acceptor or steric properties allow one to modify in a positive way, the activity and selectivity of rhodium homogeneous catalysts.

In recent years the fluorous phosphorus ligands, $P[OCH_2CH_2(CF_2)_7CF_3]_3$ and $P[CH_2CH_2(CF_2)_5CF_3]_3$, used in hydroformylation reactions as modifying ligands in novel fluorous multiphase systems demonstrated not only high stability but also a great advantage in the separation of high molecular weight aldehydes from the catalyst [36,37].

The novel amphiphilic diphosphines recently synthesised [38,39] give rise to highly active and selective hydroformylation catalysts. Rhodium complexes modified with these ligands were tested in the hydroformylation of 1-octene and were easily separated from the reaction products by acidic or basic extraction into water. Another advantage of these systems was the effective recovery of rhodium.

Some increase in selectivity (olefin isomerization low) in comparison with BISBI has been found in the application of diphosphine ligands based on heterocyclic aromatics, for example XANTPHOS [40]. The effect of modifying ligands can be

Table 2
Phosphorus mono- and bidentate ligands used for modification of rhodium hydroformylation catalysts

phospholes		 **phosphanorbornadiene**	[41–45]
	 **triphenylphosphine [46, 47]** **and derivatives after phenyl ring functionalisation**	 **triphenylphosphite [48 - 50]**	[46–50]
Fluorinated phosphine $P[CH_2CH_2(CF_2)_5CF_3]_3$			[36,37]
amphiphilic diphosphines			[38,39]
pyrrolylphosphines	 		[51]
Xantphos			[40]
zirconium diphosphosphine $\mathrm{Zr}{<}^{P}_{P}$ **or** **monophosphine** $\mathrm{Zr}{<}^{H}_{P}$			[52–56]

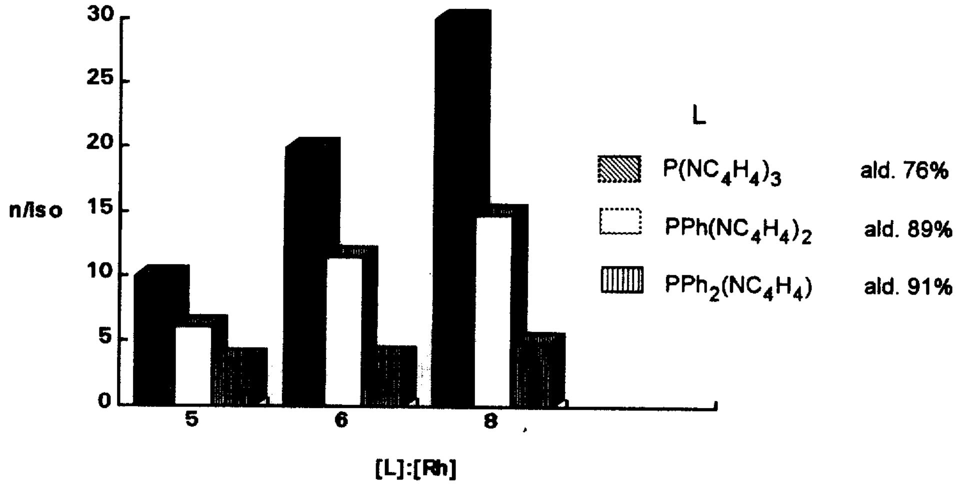


Fig. 1. Effect of *N*-pyrrolylphosphines on selectivity and yield of aldehydes in 1-hexene hydroformylation reaction (10 atm, $CO/H_2 = 1$, 60°C) [51]

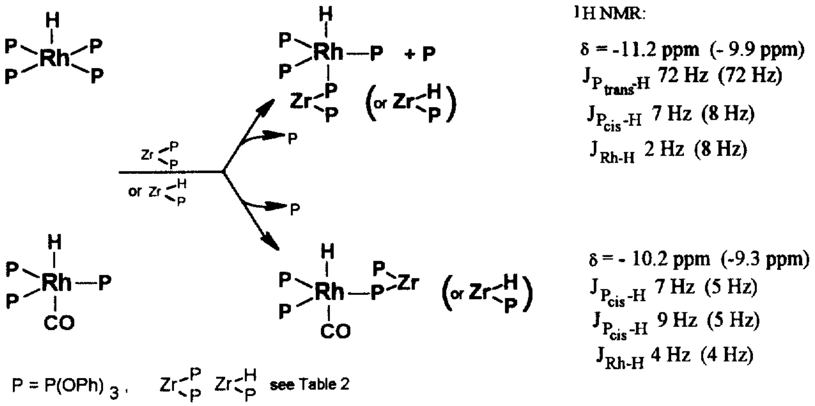
explained by the difference in bite angles and flexibility of bidentate ligands (bite angle for XANTPHOS is 111.7° and for BISBI 122.6°, whereas the corresponding flexibility range are 97–135° and 101–148°, respectively [40]).

4.1. Pyrrolylphosphines as modifying ligands

Pyrrolylphosphines of formula $P(NC_4H_4)_3$, $PPh(NC_4H_4)_2$, $PPh(NC_4H_4)$ compared with other monodentate phosphorus ligands (phosphines, phosphites, phospholes) present a broad range of donor–acceptor properties, estimated from ν_{CO} data in complexes of formula Rh(acac)(CO)P. π-acceptor properties decrease in order of decreasing value of ν_{CO} stretching frequency:

	$P(NC_4H_4)_3 >$	$PPh(NC_4H_4)_2 >$	$P(OPh)_3 >$	$PPh_2(NC_4H_4) >$	PPh_3
ν_{CO} (cm^{-1})	2012	2009	2006	2000	1975
Θ (°)	141	150	136 [57]	154	150

The cone angles (Θ) calculated from X-ray data with consideration of pyrrolyl ring rotation are almost the same for all the above mentioned ligands and similar to that of PPh_3 [51,58]. These data allow one to assume that the influence of the electronic properties of these ligands on the catalytic activity is higher than the steric properties. The results of 1-hexene hydroformylation presented in Fig. 1 illustrate this assumption and indicate that the contribution of donor and acceptor properties of $PPh(NC_4H_4)_2$ as a modifying ligand are the most efficient in achieving a high selectivity and yield of aldehydes.



Scheme 10. Bimetallic Rh(I)–Zr(IV) complexes formation.

5. Bimetallic catalytic systems

There is little literature data showing the cooperative effect of two different metal ions in catalytic systems for hydroformylation, however a positive influence of the second metal on the catalytic activity of rhodium catalysts is sometimes seen [59].

A spectacular example of such a case is observed when a Zr(IV) complex of formula $cp_2Zr(CH_2PPh_2)_2$ or $cp_2Zr(H)(CH_2PPh_2)$ is added to such rhodium(I) catalyst precursors as: $HRhP_4$, $HRh(CO)P_3$ ($P = PPh_3$, $P(OPh)_3$) or $Rh(acac)(CO)_2$ (Scheme 10). The positive effects on hydroformylation selectivity and yield of aldehydes demonstrated by Zr(IV) complexes, (which can be considered as functionalized phosphines), are shown in Table 3. ^1H-, ^{31}P-NMR studies proved the formation of intermediate catalytically active bimetallic species of formula

Table 3
Hydroformylation of 1-hexene in bimetallic Rh(I)-Zr(IV) systems

Catalyst precursor	Modifying ligand	*n*/*iso*	Σ ald.(% mol)
$HRh\{P(OPh)_3\}_4$[a]	2.0 $P(OPh)_3$	3.2	61
	2.5 HZr-P	3.5	71
	2.6 $Zr\text{-}P_2$	5.5	85
$HRh(CO)\{P(OPh)_3\}_3$[a]	1.0 $P(OPh)_3$	2.4	54
	1.5 HZr-P	3.7	75
	1.7 $Zr\text{-}P_2$	3.0	83
$(acac)Rh(CO)_2$[b]	1.69 $Zr\text{-}P_2$	1.8	85
	3.69 HZr-P	1.9	69
	1.0 $P(OPh)_3$	1.1	37
	4.0 PPh_3	2.2	80

[a] Reaction conditions: 10 atm $H_2/CO = 1$, 80°C, [1-hexene]:[Rh] = 520, [Rh] = 1.25×10^{-5} mol.
[b] Reaction conditions: 10 atm $H_2/CO = 1$, 80°C, [1-hexene]:[Rh] = 390, [Rh] = 1.4×10^{-5} mol.

Table 4
Effect of $Fe(CO)_5$ on 1-hexene hydroformylation[a]

[Rh] catalyst precursor (1.5×10^{-5} mol)	$\frac{Fe(CO)_5}{[Rh]}$	*n*+*iso* aldehydes (%)	Concentration of catalytically active forms (%)
$Rh(acac)(CO)\{P(OPh)_3\}$	0	38	65 $HRh(CO)\{P(OPh)_3\}_3$, 10 $HRh(CO)_2\{P(OPh)_3\}_2$
$Rh(acac)(CO)\{P(OPh)_3\}$	1	67	50 $HRh(CO)\{P(OPh)_3\}_3$, 50 $HRh(CO)_2\{P(OPh)_3\}_2$
	3	70	
	8	71	
$Rh_4(CO)_9\{P(OPh)_3\}_3$	0	23	Detected $HRh(CO)_2\{P(OPh)_3\}_2$
	5	72	
$Fe(CO)_5+P(OPh)_3$ used as catalyst precursor		0	

[a] Reaction conditions: 10 atm, $CO/H_2 = 1$, 80°C.

$HRh\{P(OPh)_3\}_3(cp_2Zr(CH_2PPh_2)_2)$, $HRh\{P(OPh)_3\}_3(cp_2Zr(H)CH_2PPh_2)$, $HRh\{P(OPh)_3\}_2(CO)(cp_2Zr(CH_2PPh_2)_2)$ and $HRh\{P(OPh)_3\}_2(CO)(cp_2Zr(H)CH_2PPh_2)$ (Scheme 10).

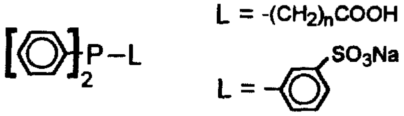
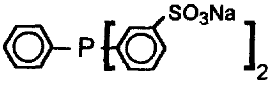
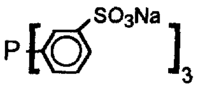
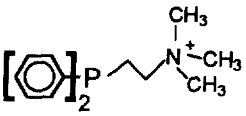
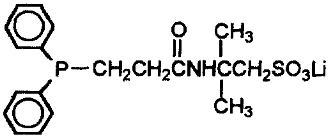
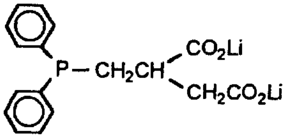
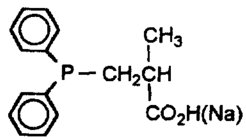
Recently we have found [24] an unexpected positive effect of $Fe(CO)_5$ on the catalytic activity of rhodium systems with a low ratio of phosphorus ligand to rhodium ([P]:[Rh] ca. 1). Iron carbonyl itself does not catalyse hydroformylation, however in combination with a rhodium catalyst precursor it significantly accelerates the rate of hydroformylation and increases the yield of aldehydes if compared to the system free of $Fe(CO)_5$ (Table 4). According to ^1H-, ^{31}P-NMR studies, the addition of $Fe(CO)_5$ increases the concentration of catalytically active complex $HRh(CO)_2\{P(OPh)_3\}_2$ with simultaneous formation of $Fe(CO)_4\{P(OPh)_3\}$.

In an experiment with $Rh_4(CO)_9\{P(OPh)_3\}_3$, which itself is weakly active, after addition of $Fe(CO)_5$ an increase of hydroformylation reaction yield and a decrease of isomerization of 1-hexene to 2-hexene were observed. In both systems the addition of $Fe(CO)_5$ stabilizes the concentration of $HRh(CO)_2\{P(OPh)_3\}_2$ and prevents its transformation to the less active and soluble $Rh_4(CO)_x\{P(OPh)_3\}_y$ ($x = y = 12$) species.

6. Water soluble phosphines as modifying ligands

An important and stimulating advantage of the application of the new ligand to the hydroformylation reaction was the success in elaboration and application of water soluble phosphorus ligands which allow the very easy separation of organic products from water soluble catalysts, especially important in processes of higher olefin hydroformylation. Additionally, high reaction rates and selectivities can be obtained in biphasic media.

Table 5
Examples of water soluble phosphorus ligands

	TPPMS	[61–63] [64–66]
	TPPDS	[67,68]
	TPPTS	[8,67]
		[69–71]
	PNS	[72–74]
	PC	[73]
	PH (PNa)	[73]

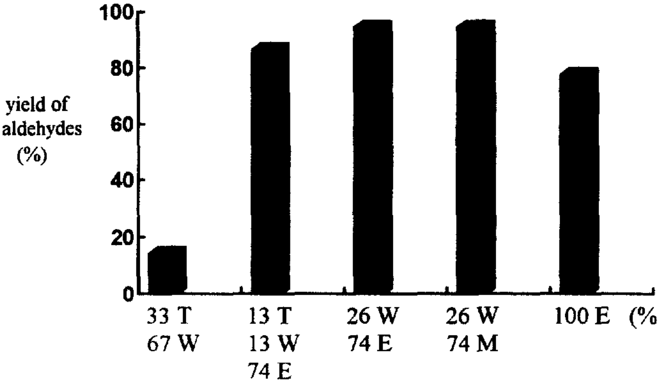


Fig. 2. Effect of mixed solvent composition on the reaction yield of 1-hexene hydroformylation [73]. T, toluene; W, water; E, ethanol; M, methanol.

Table 5 lists some water soluble phosphorus ligands (mono- and bidentate) used effectively in homogeneous catalysis. The application of a water soluble catalyst was successful industrially and was implemented as the Ruhrchemie/Rhone Poulenc process. The reactive form of the catalyst, $HRh(CO)(TPPTS)_3$ was found to be more resistant against decomposition compared with corresponding systems based on triphenylphosphine [60].

New water soluble phosphines of formula $Ph_2PCH_2CH_2C(O)NHC(CH_3)_2CH_2SO_3Li$ (PNS), $Ph_2PCH_2CH(COOLi)(CH_2COOLi)$ (PC), $Ph_2PCH_2CH(CH_3)(COOH)$ (PH) and $Ph_2PCH_2CH(CH_3)(COONa)$ (PNa) were successfully applied for the modification of rhodium based catalytic systems for hydroformylation of methyl acrylate [72], 1-hexene [73] and C_4 unsaturated alcohols [74]. These phosphines may compete with TPPTS, presenting reasonable stability at higher pH.

The hydroformylation of 1-hexene in the $Rh(acac)(CO)_2$/PNS system in the mixed solvents (toluene–water–ethanol) shows a strong dependence of the reaction yield on solvent composition (Fig. 2).

The catalytic system $Rh(acac)(CO)_2$/PNS applied to C_4 unsaturated alcohol hydroformylation shows the highest activity towards terminal double bonds (over 90% of aldehydes) and lower activity with respect to alcohols with internal double bonds (ca. 70% of aldehydes). The reaction may be carried out only in aqueous solution and conversion of the substrates strongly depends on pH which is demonstrated for the less reactive substrate 2-buten-1-ol (Fig. 3) [74].

From the data presented in Table 6 it can be concluded that the transformation of a hydrophobic phosphine into a hydrophillic water soluble ligand causes a significant increase in hydroformylation reaction selectivity—for example the *n*/*iso* factor increases from 2.5–12.5 for PPh_3 [46,47] to ≥ 15 for TPPTS [8,78]. Similarly, the increase in *n*/*iso* from 19 for NAPHOS [75] to over 50 for BINAS [76,77] was observed (Table 6).

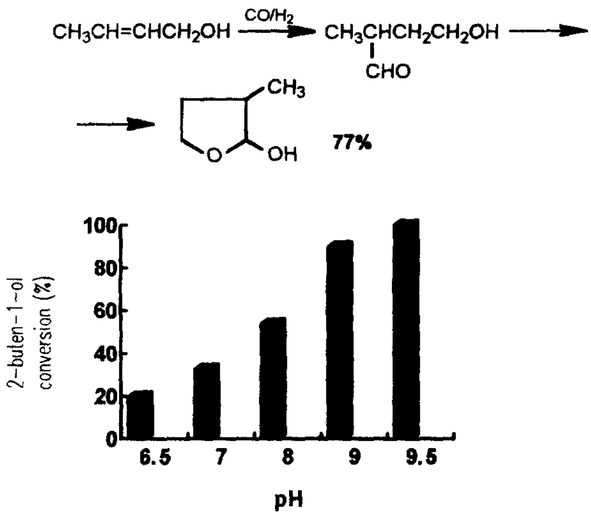
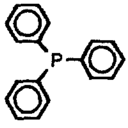
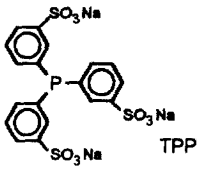
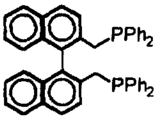
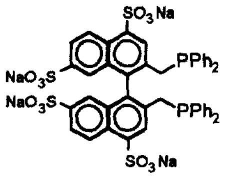
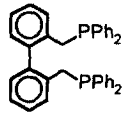
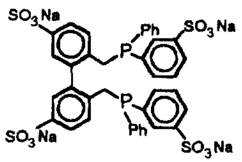


Fig. 3. Effect of pH on conversion of 2-buten-1-ol into 2-hydroxy-3-methyl-tetrahydrofuran.

Table 6
Effect on selectivity of bidentate modifying phosphorus ligands compared with that of PPh_3 and TPPTS in 1-hexene hydroformylation

Hydrophobic P-ligands	selectivity n/iso		Hydrophillic P-ligands
 PPh_3 [46, 47]	2.5 -12.5	15.7	 TPPTS [8, 78]
 NAPHOS [75]	19	49 - 99	 BINAS [76, 77]
 BISBI [77]	24	32.3	 BISBIS [76]

7. Prospects of hydroformylation

This discussion has described the present state of the hydroformylation process. In spite of the high level of implemented commercial processes, hydroformylation still has a large capacity for development, both for research and for applications. There are still some possibilities to improve existing excellent industrial processes, to make them simpler and more environmentally friendly. This tendency is demonstrated when the LPO process invented by Union Carbide is compared with biphasic process implemented by Ruhrchemie/Rhone Poulenc. The further improvement of catalytic activity of systems based on water soluble phosphorus ligands or bimetallic homogeneous catalysts will open interesting and promising perspectives for rhodium chemistry.

The new generation of modifying ligands, especially bulky phosphites, will allow one to design new active and selective catalysts. Rhodium organometallic complexes with powerful ligands will allow one to design homogeneous catalysts fulfilling all the requirements with respect to their application to hydroformylation of long chain and functionalized olefins including asymmetric hydroformylation not discussed in this review.

References

[1] O. Roelen, DE 849 548 (1938/1952), Chemische Verwertungsgesellschaft mbH, Oberhausen.
[2] J. Falbe (Ed.), New Syntheses with Carbon Monoxide, Springer–Verlag, New York, 1980.
[3] I. Tkatchenko, in: G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, vol. 8, Pergamon Press, Oxford, 1982, p. 101.
[4] R.L. Pruett, Adv. Organomet. Chem. 17 (1979) 1.
[5] B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Two Volumes, VCH–Weinheim, New York/Basel/Cambridge/Tokyo, 1996.
[6] C.P. Casey, L.M. Petrovich, J. Am. Chem. Soc. 114 (1992) 5535.
[7] R.L. Pruett, US Pat. 3,499,932, (1967), Union Carbide.
[8] B. Cornils, E.G. Kuntz, J. Organomet. Chem. 502 (1995) 177.
[9] J.A. Godfrey, R.A. Searles, Chem. Technik 10 (1981) 1271.
[10] B. Cornils, L. Marko, Methoden der Organischen Chemie (Houben-Weyl), Georg Thieme Verlag, Stuttgart, New York, 1986.
[11] K.H. Schmidt, Chem. Ind. 108 (1985) 762.
[12] D.E. Bryant, E. Billig, US Pat. 4,277,627 (1981), Union Carbide.
[13] A.G. Abatjoglou, E. Billig, D.R. Bryant, Organometallics 3 (1984) 923.
[14] A.G. Abatjoglou, D.R. Bryant, Organometallics 3 (1984) 932.
[15] R.M. Deshpande, S.S. Divekar, R.V. Gholap, R.V. Chaudhari, J. Mol. Catal. 67 (1991) 333.
[16] R.A. Dubois, Organometallics 3 (1984) 649.
[17] M. Beller, B. Cornils, C.D. Frohning, C.W. Kohlpaintner, J. Mol. Catal. A Chem. 104 (1995) 17.
[18] W.A. Herrmann, C.W. Kohpaintner, Angew. Chem. Int. Ed. Engl. 32 (1993) 1524.
[19] W. Keim, J. Organomet. Chem. 14 (1968) 179.
[20] G. Wilkinson, M. Yagupsky, C.K. Brown, G. Yagupsky, J. Chem. Soc. A (1970) 937
[21] E.K. Barefield, G.W. Parshall, Inorg. Chem. 11 (1972) 964.
[22] G.W. Parshall, W.H. Knoth, R.A. Schunn, J. Am. Chem. Soc. 91 (1969) 4990.
[23] H.K.A.C. Coolen, R.J.M. Nolte, P.W.N.M. van Leeuwen, J. Organomet. Chem. 496 (1995) 159.

[24] A.M. Trzeciak, J.J. Ziólkowski, unpublished results.
[25] A.M. Trzeciak, J.J. Ziólkowski, Trans. Met. Chem. 10 (1985) 385.
[26] A.M. Trzeciak, J.J. Ziólkowski, Z. Anorg. Allg. Chem. 577 (1989) 255.
[27] A.M. Trzeciak, J.J. Ziólkowski, K. Mereiter, unpublished results
[28] E. Billig, Eur. Pat. Appl. EP 214,622 (1987); US Pat. 4,769,498, Union Carbide.
[29] E. Billig, A.G. Abatjoglou, D.R. Bryant, Eur. Pat. Appl. EP 213,693 (1987); US Pat. 4,748,261, Union Carbide.
[30] E. Billig, A.G. Abatjoglou, D.R. Bryant, R.E. Murray, M.J. Maher, PCT Int. Appl. WO 8503,702 (1985); US Pat. 4,789,753, Union Carbide.
[31] M.P. Lorz, W.Bertleff, M. Roeper, D. Koeffer, Eur. Pat. Appl. EP 472,071 (1992), BASFA.-G.
[32] P.W.N.M. van Leeuwen, G.F. Roobeek, Eur. Pat. Appl. EP 34,986 (1982) and GB Appl 80/41,098 (1980), Shell.
[33] T.J. Devon, G.W. Phillips, T.A. Puckette, J.L. Stavinoha, J.J. Vanderbilt, US Pat. 4,694,109, Kodak.
[34] D.R. Bryant, 203rd American Chemical Society, National Meeting, San Francisco, CA, 1992.
[35] D.R. Bryant, E. Billig, 4th International Conference on The Chemistry of the Platinum Group Metals, Cambridge, 1990.
[36] I.T. Horvath, I. Rabai, Science 266 (1994) 72.
[37] I.T. Horvath, I. Rabai, US Pat., 5 463 082 (1995), Exxon.
[38] A. Buhling, J.W. Elgersma, S. Nkrumah, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Chem. Soc. Dalton Trans. (1996) 2143
[39] A. Buhling, P.C.J. Kamer, P.W.N.M. van Leeuwen, J.W. Elgersma, J. Mol. Catal. 116 (1997) 297.
[40] M. Kranenburg, Y.E.M. van der Burgt, P.C.J. Kamer, P.W.N.M. van Leeuwen, K. Goubitz, J. Fraanje, Organometallics 14 (1995) 3081.
[41] J. Hjotkjaer, P. Toromanova-Petrova, J. Mol. Catal. 50 (1989) 203.
[42] D. Neibecker, R. Reau, J. Mol. Catal. 53 (1989) 219.
[43] D. Neibecker, R. Reau, J. Mol. Catal. 57 (1989) 153.
[44] D. Neibecker, R. Reau, Angew. Chem. Int. Ed. Engl. 28 (1989) 500.
[45] D. Neibecker, R. Reau, New J. Chem. 15 (1991) 279.
[46] D. Evans, J.A. Osborn, G. Wilkinson, J. Chem. Soc. A (1968) 3133.
[47] C.K. Brown, G. Wilkinson, J. Chem. Soc. A (1970) 2753.
[48] R.L. Pruett, J.A. Smith, J. Org. Chem. 34 (2) (1969) 327.
[49] A.M. Trzeciak, J.J. Ziólkowski, J. Mol. Catal. 48 (1988) 319.
[50] A.M. Trzeciak, J.J. Ziólkowski, J. Organomet. Chem. 464 (1994) 107.
[51] A.M. Trzeciak, T. Glowiak, R. Grzybek, J.J. Ziólkowski, J. Chem. Soc. Dalton Trans. (1997) 1831.
[52] R. Choukroun, A. Iraqi, D. Gervais, J. Organomet. Chem. 311 (1986) C60.
[53] R. Choukroun, D. Gervais, P. Kalck, F. Senocq, J. Organomet. Chem. 335 (1987) C9.
[54] A.M. Trzeciak, J.J. Ziólkowski, R. Choukroun, J. Organomet. Chem. 420 (1991) 353.
[55] A.M. Trzeciak, J.J. Ziólkowski, R. Choukroun, J. Organomet. Chem. 525 (1996) 145.
[56] A.M. Trzeciak, J.J. Ziólkowski, R. Choukroun, J. Mol. Catal. A Chem. 110 (1996) 135.
[57] C.A. Tolman, Chem. Rev. 77 (1977) 313.
[58] K.G. Moloy, J.L. Petersen, J. Am. Chem. Soc. 117 (1995) 7696.
[59] P. Braunstein, J. Rose, in: E.W. Abel, F. Gordon, A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, vol. II, Pergamon, Oxford, 1995.
[60] I.T. Horvath, R.V. Kastrup, A.A. Oswald, E.J. Mozeleski, Catal. Lett. 2 (1989) 85.
[61] F.G. Mann, I.T. Millar, J. Chem. Soc. (1952) 4453
[62] L.D. Pettit, H.N.M.H. Irving, J. Chem. Soc. (1964) 5336
[63] T. Jarolim, J. Podlahova, J. Inorg. Nucl. Chem. 38 (1) (1976) 125.
[64] S. Ahrland, J. Chatt, N.R. Davies, A.A. Wiliams, J. Chem. Soc. 276 (1958) 276.
[65] F. Joo, M.T. Beck, React. Kinet. Catal. Lett. 2 (1975) 257.
[66] A.F. Borowski, D.J. Cole-Hamilton, G. Wilkinson, Nouv. J. Chem. 2 (1978) 137.
[67] E. Kuntz, Chemtech 17 (9) (1987) 570.
[68] Y. Tokito, N. Yoshimura, JP 62.030.734 (1987), Kuraray Corporation.
[69] R.T. Smith, K.U. Ungar, M.C. Baird, Trans. Met. Chem. 7 (1982) 288.

[70] R.T. Smith, K.U. Ungar, L.J. Sanderson, M.C. Baird, Ann. N.Y. Acad. Sci. 415 (1983) 253.
[71] R.T. Smith, K.U. Ungar, L.J. Sanderson, M.C. Baird, Organometallics 2 (1983) 1137.
[72] G. Fremy, Y. Castanet, R. Grzybek, E. Monflier, A. Mortreux, A.M. Trzeciak, J.J. Ziółkowski, J. Organomet. Chem. 505 (1995) 11.
[73] E. Mieczyñska, A.M. Trzeciak, R. Grzybek, J.J. Ziółkowski, J. Mol. Catal. A Chem. 132 (1998) 203.
[74] E. Mieczyñska, A.M. Trzeciak, J.J. Ziółkowski, J. Mol. Catal. A Chem. (1999), in press.
[75] K. Tamao, Y. Yamamoto, H. Matsumoto, N. Miyake, M. Kumada, Tetrahedron Lett. 16 (1977) 1389.
[76] W.A. Herrmann, C.W. Kohlpaintner, R.B. Manatsberger, H. Bahrmann, H. Kottmann, J. Mol. Catal. A Chem. 97 (1995) 65.
[77] M. Beller, B. Cornils, C.D. Frohling, C.W. Kohlpaintner, J. Mol. Catal. A Chem. 104 (1995) 17.
[78] H. Bahrmann, H. Bach, C.D. Frohling, H.J. Kleiner, P. Lappe, D. Peters, D. Regnat, W.A. Herrmann, J. Mol. Catal. A Chem. 116 (1997) 49.