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Application of transition metals in hydroformylation Annual survey covering the year 1997

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Contents

Abstract

Hydroformylation in homogeneous and heterogeneous systems and hydroformylation related reactions of carbon monoxide are reviewed. © 1998 Elsevier Science S.A.

Keywords: Hydroformylation; Water–gas shift reaction; Reduction of carbon monoxide; Reduction of carbon dioxide; Transition metals

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1. Hydroformylation

1.1. Homogeneous systems

1.1.1. Cobalt catalysts

Propylene hydroformylation in supercritical carbon dioxide at 66–108 °C and 93–186 bar using $Co_2(CO)_8$ as the precatalyst was studied. It was found that the observed rate constant increased with pressure and the linear/branched aldehyde product selectivity at 88 °C increases from 2.7 to 4.3 as the pressure doubles from 93 to 186 bar [1,2].

The rate of hydroformylation of cyclohexene to cyclohexanecarboxaldehyde in the presence of $Co_2(CO)_8$ at 100 °C was found to be strongly reduced by the presence of N_2 or Ar under very high pressure. Thus, the conversion of cyclohexene at $P(CO) = 70 \pm 1$ bar and $P(H_2) = 85 \pm 2$ bar in 3 h dropped from 30% to 12% or 9% by using an additional pressure of 1039 bar N_2 or 1015 bar Ar, respectively. Competition of N_2 or Ar with H_2 and/or the olefin within the coordination sphere of the catalytically active cobalt carbonyl species was suggested to be responsible for the observed behavior [3].

The effect of the catalyst precursor $Co_2(CO)_8 + RCOOH$ and $Co(RCOO)_2$ on the rate of propylene hydroformylation was studied [4,5]. The effect of substrate and catalyst concentration on the rate of hydroformylation of a butane–butene distillation fraction using $Co(RCOO)_2$ as the catalyst precursor was investigated [6,7]. The kinetics of the cobalt-catalyzed isobutylene hydroformylation were studied using $Co(RCOO)_2$ as the catalyst precursor. The effects of the isobutylene and cobalt concentrations on the rates were evaluated [8,9]. The kinetics of the hydroformylation of 1-hexene using cobalt heptanoate as a catalyst precursor were studied. The reaction was found to be first order in substrate, and the rate increased linearly with the cobalt concentration [10,11].

The reaction behavior of dienes in the C_5 by-product fraction from ethylene manufacturing was investigated and compared with that of monoenes. Hydroformylation of linear conjugated dienes produces saturated primary alcohols, whereas cyclopentadiene temporarily poisons the catalyst. Hydroformylation of a cyclopentadiene-free C_5 fraction at 50–60 bar $CO{:}H_2 = 1{:}2$ at 180 °C resulted in a 92% yield of alcohols [12,13]. High pressure in situ IR investigation has shown that isoprene is first hydrogenated and then hydroformylated to hexanal. Cyclopentadiene coordinates with the cobalt–phosphine catalyst leading to $C_5H_5Co(CO)_2$ [14,15]. The electronic effects of phosphine ligands on the stability and activity of $HCo(CO)_3L$ in hydroformylation were studied by high pressure in situ IR spectroscopy. The experimental results indicate that the stability of $HCo(CO)_3L$ and the hydroformylation activity of the cobalt phosphine catalysts are increased with increase of electron donor ability of the ligands [16,17].

Hydroformylation versus hydrocarboxylation of cyclohexene under homogeneous water–gas shift reaction conditions was studied using the octacarbonyldicobalt/1,2-diphenylphosphinoethane/THF–water system. Using this catalytic system, cyclohexene with carbon monoxide and water gives cyclohexanecarboxaldehyde and cyclohaxanecarboxylic acid as the main reaction products and cyclohexylmethanol as by-product. The effects of the reaction variables such as water concentration, reaction temperature, carbon monoxide pressure and catalyst concentration on the product ratios were investigated [18].

1.1.2. Rhodium catalysts

2-(Trifluoromethyl)propanal was prepared in 90% yield by rhodium-catalyzed hydroformylation of 3,3,3-trifluoropropene [19,20].

In situ IR spectroscopy has been used to follow the formation of octanal and octanol in rhodium-catalyzed hydroformylation of 1-heptene using the $Rh_2(OAc)_4$ and the $Rh_6(CO)_{16}/PBu_3/EtOH$ systems [21,22].

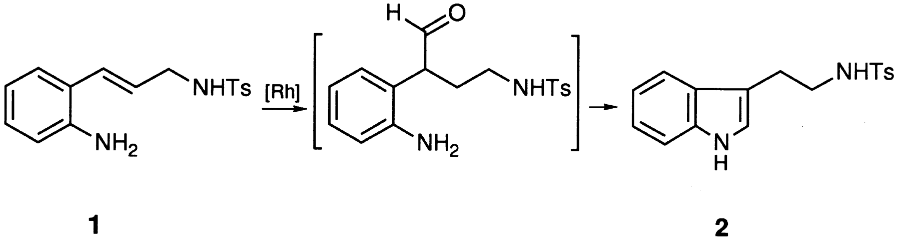
A dissertation dealing with modeling, simulation, and advanced control of a rhodium-catalyzed propylene hydroformylation process was reported [23,24].

Homogeneous catalytic hydroformylation of a styrene–butadiene copolymer was examined using a rhodium catalyst precursor containing 1,5-cyclooctadiene and other ligands. Under a total pressure of 50 bar CO/H_2 at 40 °C, $[Rh(COD)_2]BF_4$ and $[Rh(COD)Cl]_2$ were found to be more active than $HRh(CO)(PPh_3)_3$, $[Rh(COD)dppb]BF_4$, or $[Rh(COD)]BF_4$. Full conversion of polyolefin was achieved using $[Rh(COD)_2]BF_4$ and $[Rh(COD)Cl]_2$ as the catalyst [25,26].

A batch process for the hydroformylation of isobutene was developed for the production of isovaleraldehyde using a non-phosphine $Rh(CO)_2(acac)$ system at extremely low levels of rhodium [27,28].

Hydroformylation of 2,4,4-trimethyl-1-pentene was studied between 27–127 °C at 20–120 bar $CO/H_2 = 1$ using $Na_2[Rh_{12}(CO)_{30}]$ as the catalyst precursor. In the highly chemoselective reaction the 3,5,5-trimethylhexanal formation approaches 100%. Typical turnover numbers are 100–1000 mol olefin/mol cluster [29].

Rhodium-catalyzed hydroformylation of functionalized anilines was applied in the synthesis of triptamines and triptols in 32–73% yield. E.g.: the hydroformylation of **1** at 70 °C and 20 bar $CO:H_2 = 1:1$ in toluene in the presence of 5 mol% $HRh(CO)(PPh_3)_3$, the corresponding triptamine **2** was formed in one step in 58% yield [30].

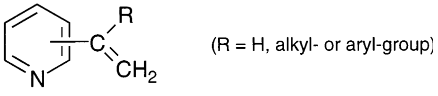


1 **2**

The kinetics of the $HRh(CO)(PPh_3)_3$-catalyzed hydroformylation of 1-dodecene in toluene were investigated in a temperature range of 50–70 °C. The rate of hydroformylation was found to be first order with respect to catalyst concentration and to the partial pressure of dihydrogen, and negative first order with respect to the carbon monoxide partial pressure. The order with respect to 1-dodecene was found to be dependent on the concentration range. First order was observed in the lower concentration range (0.18–0.36 M) and zero order in the higher concentration range (0.36–2.2 M) [31].

Rhodium carbonyl complex catalyst systems with the lithium salt of triphenylphosphine–monosulfonic acid as complex ligand have been used in homogeneous hydroformylation of unsaturated fatty compounds such as methyl linoleate in methanol. A novel homogeneous–heterogeneous procedure was applied for the recycling of the catalyst. After the reaction methanol is distilled off and the precipitated catalyst system is dissolved in water and separated from the hydroformylation products. After evaporation of the water the catalyst system is redissolved in methanol and returned into the process without any loss of catalytic activity [32–35].

Hydroformylation of vinylpyridine derivatives **3** was studied using homogeneous rhodium catalysts in benzene solution at 80 °C and 90–100 bar of $CO:H_2 = 1:1$ with respect to the regioselectivity of the aldehyde formation. In the case of 1′-alkyl- or 1′-aryl-2-vinylpyridine hydroformylation occurs with the exclusive formation of the more branched aldehyde, whereas in the case of aryl-substituted 1′-aryl-4-vinylpyridine only the more linear aldehyde was observed [36].



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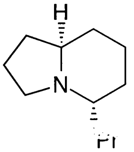
Regioselective rhodium-catalyzed hydroformylation of olefinic pyrrolidine derivatives was utilized as a key step in the synthesis of alkaloids, such as **4** and **5** [37,38].



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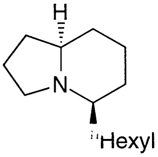

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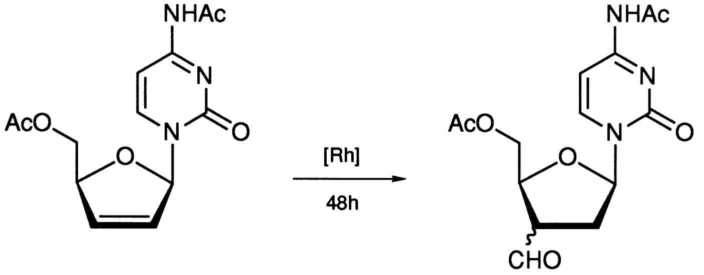
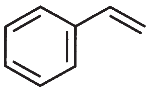
Hydroformylation of 2′,3′-didehydro-2′,3′-dideoxycytidine (**6**) at 60 °C and 5 bar $CO:H_2 = 1:1$ in dry THF in the presence of $Rh(CO)_2(acac)$ and PPh_3 as the catalyst precursors gave **7** as the main product in 32% yield [39]. This novel rhodium-catalyzed reaction was used to prepare 2′,3′-dideoxy-3′-hydroxymethylcytidine, a unique anti-viral nucleoside, in four steps from **6** [40,41].

Enantioselective hydroformylation of vinyl aromatics (**8–12**) using a rhodium complex with **13** as the ligand was investigated at 80 °C. Good aldehyde yields with prevalent formation of the branched aldehyde were obtained, but the enantioselectivities were low to moderate, up to 45% *ee* [42].

Rhodium perfluorobenzenethiolato complexes $(C_5Me_5)Rh(SR_F)_2$ ($R_F = C_6F_5$;



6 **7**



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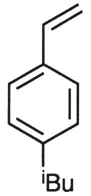

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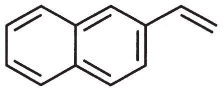

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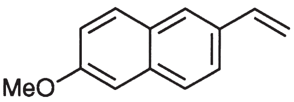

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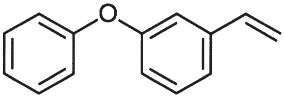

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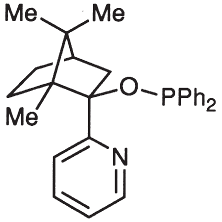

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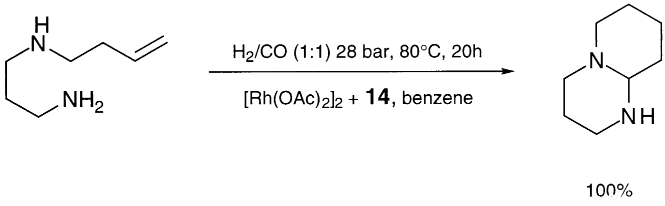
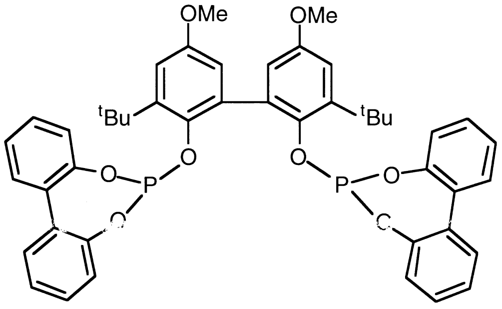
p-C_6F_4H) in the presence of triphenylphosphine were studied as catalyst precursors for the hydroformylation of 1-hexene in toluene at 5 and 30 bar at 80 °C. No conversion to aldehydes was obtained in the absence of triphenylphosphine, and practically no conversion was observed at 5 bar $CO{:}H_2 = 1{:}1$. After long induction periods at 30 bar and using molar ratios of PPh_3:complex = 2 or 3, 78% conversion in 24 h was achieved. Only linear and branched aldehydes were formed with 73/27 ratio without any hydrogenation and isomerization side products [43]. Perfluorothiolate compounds $[Rh(\mu\text{-}SC_6F_5)(COD)]_2$ and $[Rh(\mu\text{-}SC_6F_5)(CO)_2]_2$ in combination with PPh_3 were studied as catalyst precursors for the hydroformylation of 1-heptene in toluene at 30 bar and 70 °C. In comparison with monomeric rhodium complexes, the dimeric complexes gave enhanced selectivity towards the linear aldehyde [44]. A rhodium catalyst modified with tris(2-*tert*-butyl-4-methylphenyl)phosphite was used for the hydroformylation of unsaturated fatty acid esters. This phosphite-modified catalyst was found to be more active than the classic triphenylphosphine-modified catalyst. With methyl oleate 400–500 mol/mol/h turnover numbers were achieved at 80–100 °C, 20 bar CO:H_2 = 1:1 in toluene (substrate/rhodium ratio = 910) with ~95% conversion in 3 h. With technical grade methyl oleate containing 14% 9,12-diene and methyl linoleate, lower reaction rates were found because some stable π-allylic intermediates were formed, which slowly undergo hydroformylation [45,46].

The rhodium-catalyzed reactions of *N*-allyl- and *N*-butenyl-1,3-diaminopropanes were found to give single products arising from exclusive hydroformylation at the terminal carbon when the hindered bisphosphite ligand BIPHEPHOS (**14**) is used [47]. E.g.:





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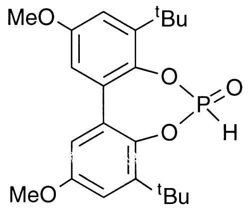
A catalyst formed in situ from Rh(hfacac)(η^4-C_8H_{12}) and (3-CF_3-$(CF_2)_5(CH_2)_2C_6H_4)_3P$ was found to catalyze the hydroformylation of 1-octene in supercritical CO_2 at 60 °C and 220 bar to the isomeric aldehydes nonanal and 2-methyloctanal (4.6/1 ratio) with 92% conversion and no side reaction [48].

Mixed phosphito-phosphonato rhodium(I) complexes with **15** as the ligand were found to act as catalyst precursors for the hydroformylation of styrene and 2-vinyl naphthalene. Based on comparison of rates it was concluded that the precursors lose the phosphorus-containing moieties under catalytic hydroformylation conditions to give unsubstituted hydridorhodium carbonyl as the catalytically active species [49].

The novel amphiphilic ligands **16–18** have been found to be active and highly



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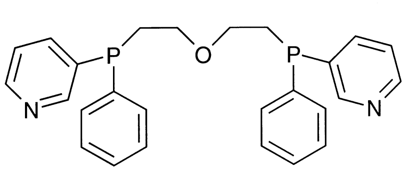
selective in the rhodium-catalyzed hydroformylation of 1-octene at 80 °C and 20 bar of $CO:H_2 = 1:1$ in toluene. Linear:branched aldehyde ratios of 50 have been achieved. Rhodium recycling experiments using **17** and **18** show that rhodium can be extracted into an aqueous layer at pH 5–5.5 for more than 99.95% [50].



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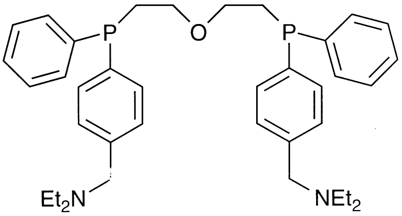

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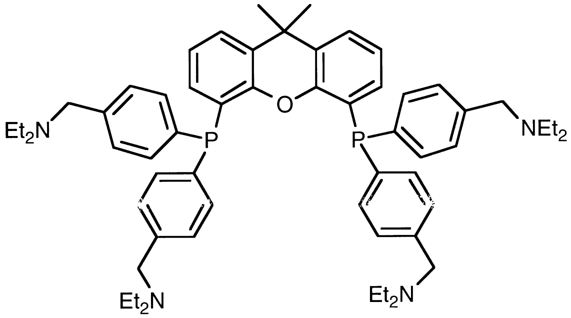
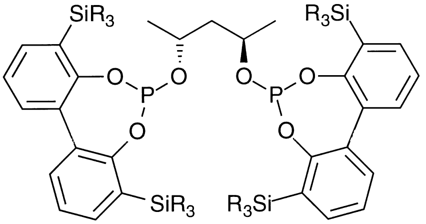


18

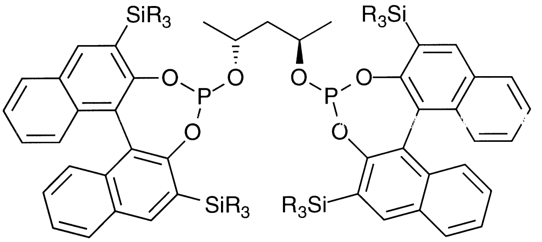
The performance of a new rhodium recycling system was described using a series of amphiphilic ligands: Ph_2ArP (Ar = 3-hydroxyphenyl, 4-carboxyphenyl), $Ph_nAr_{3-n}P$ ($Ar = 4\text{-}PhCH_2X$, $X = NEt_2$, NMePh, NPh_2; $n = 1$, 2) and $Ph_nAr_{3-n}P$ (Ar = 3-pyridyl, 4-pyridyl; $n = 1$, 2). The corresponding rhodium complexes were found to be active in the hydroformylation of 1-octene and could be separated from the product aldehydes by acidic or basic extraction into water. After neutralization of the aqueous phase the rhodium phosphine complexes could be extracted into a new batch of 1-octene, with toluene as organic solvent. Pressurizing the recovered rhodium and excess ligand to 20 bar syn gas at 80 °C resulted in regeneration of the catalytic activity up to 87% of the original one [51].

Variation of the ortho substituents on the biphenol or binaphthol moieties in diphosphites **19–23** was found to have a large effect on the asymmetric induction of the rhodium-catalyzed asymmetric hydroformylation of styrene.



(R = Me, Et, Ph)

19-21

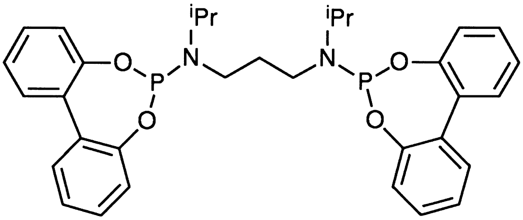


(R_3 = ${}^{t}BuMe_2$; Me_3)

22-23

The highest selectivity (87% *ee* and 95% regioselectivity for 2-phenylpropanal) was obtained with trimethylsilyl substituents at the ortho position under mild reaction conditions (25 °C, 20 bar of syn gas $CO/H_2=1$). The solution structures of the active catalysts HRh(diphosphite)$(CO)_2$ complexes were studied by ^{31}P and ^{1}H NMR spectroscopy at variable temperature. Spectroscopic data, in combination with the obtained results in catalysis, suggest that diphosphite ligands containing the conformationally flexible axially chiral biphenyl moieties predominantly exist as single atropisomers in the HRh(diphosphite)$(CO)_2$ complexes [52].

Phosphoramidites such as **24** were applied as ligands in the rhodium-catalyzed hydroformylation of 1-octene and styrene. Using ligand **24** with combination of (acetylacetonate)dicarbonylrhodium a maximum rate of 1200 mol/mol Rh · h for 1-octene was observed at 80 °C and 20 bar $CO:H_2=1:1$ with 91% regioselectivity for linear product. Under the same conditions, but at 40 °C for styrene, up to 25 mol/mol Rh · h rate was observed with selectivities for branched aldehyde of 89%. Characterization of the rhodium complexes has shown that ligand **24** is coordinated bis-equatorially in the trigonal bipyramidal rhodium complex, which accounts for the high regioselectivities [53,54].



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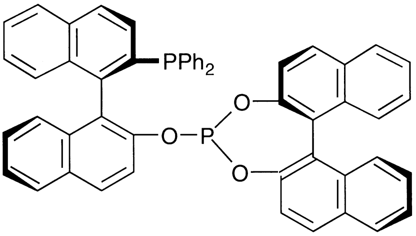
Rhodium(I) complexes with *N*-pyrrolylphosphine ligands ($P(C_4H_4N)_{3-n}Ph_n$; $n=$ 0, 1, 2) were found to be precursors of very active and selective hydroformylation catalysts, which at 60 °C and 10 bar $CO:H_2=1:1$ produce 80–90% of aldehydes with n:iso ratios of 3–31:1 [55]. Rhodium(I) complexes of chiral phosphine–phosphites such as (*R*,*S*)-BINAPHOS (**25**) were found to be highly effective catalysts for asymmetric hydroformylations of a wide range of prochiral olefins including heteroatom-functionalized olefins and 1,2-disubstituted olefins. The observed enantiomeric excess for styrene and its derivatives is 88–95%, for vinyl carboxylates 80–98%, for *N*-vinylphthalimide 85%, for vinyl 4-methylphenyl sulfide 74%, for 3,3,3-trifluoropropene 92%, for (*E*)-1-propenylbenzene 92%, for monosubstituted aliphatic olefins 82–83%, and for 1-vinylcyclohexene 96%. The reason for the exceptionally high enantioselectivities has been attributed to the exclusive formation of a single active species, $RhH(CO)_2$(phosphine–phosphite) in which the phosphine occupies the equatorial position and the phosphite the apical position [56].



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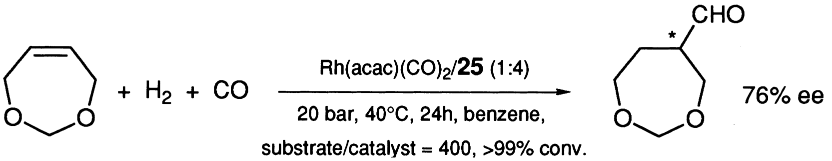
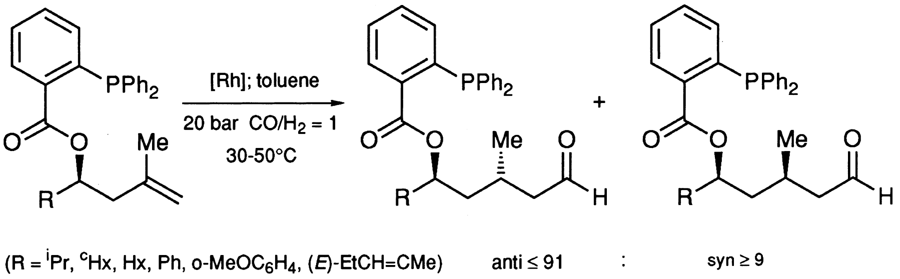
Mechanistic aspects of asymmetric hydroformylation of 1-hexene and styrene were examined using the rhodium(I) complex of **25** as the catalyst at different CO and H_2 partial pressures ($p(H_2)$, $p(CO)=5$–50 bar). For both substrates, the higher CO partial pressure inhibits the reaction, but the variation of the H_2 partial pressure has almost no effect on the reaction rate. In most cases no significant change in the regio- and enantioselectivities was observed with variation of the H_2 and CO pressure. From deuteroformylation experiments (30–60 °C, 20–100 bar $D_2:CO=1:1$) it was concluded that the olefin-insertion step is irreversible and the regio- and enantioselectivity under these conditions is controlled by the olefin insertion step [57]. Asymmetric hydroformylation of heterocyclic olefins catalyzed by phosphine–phosphite–rhodium(I) complexes was investigated. Hydroformylation of symmetrical heterocyclic olefins such as 2,5-dihydrofuran, 3-pyrroline derivatives, and 4,7-dihydro-1,3-dioxepin derivatives afforded the optically active aldehydes as single products in 64–76% *ee*. E.g.:



Unsymmetrical substrates such as 2,3-dihydrofuran and *N*-(*tert*-butoxycarbonyl)-2-pyrroline gave a mixture of regioisomers [58]. Chiral γ-butyrolactones were synthesized by the asymmetric hydroformylation of allylic alcohols catalyzed by a rhodium(I) complex of **25**, followed by silver(I) oxidation [59,60]. Asymmetric hydroformylation of conjugated dienes was investigated using the rhodium(I) complex of **25** as the catalyst. Optically active β,γ-unsaturated aldehydes were obtained in high regio- (78–94%) and enantioselectivities (80–97% *ee*) from 1-vinylcyclohexene, 4-methyl-1,3-pentadiene, and (*E*)-1-phenyl-1,3-butadiene. On the other hand, hydroformylation of 1,3-butadiene gave achiral product, (*E*)- and (*Z*)-3-pentanal in up to 95% selectivity [61,62].

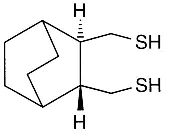
High 1,3-asymmetric induction in the rhodium-catalyzed hydroformylation of homomethallylic alcohols was achieved by use of *o*-diphenylphosphinobenzoic acid as an effective catalyst directing group. Thus, homomethallylic *o*-diphenylphosphinobenzoic acid esters (**26**) were subjected to hydroformylation conditions using 0.7 mol% of Rh(CO)$_2$(acac)–P(OPh)$_3$ as the catalyst precursor resulting in the corresponding aldehydes (**27**) in good to excellent yields and with anti-diastereoselectivities of up to 91% [63].



26 **27**

Hydroformylation and enantioselective hydroformylation of 1-(4′-methoxyphenyl)-propene and 3-(4′-methoxyphenyl)-propene with in situ rhodium and platinum complex catalysts have been studied. While α- and β-substituted formyl regioisomers were formed in the hydroformylation of the propenylarene by rhodium catalysts, all three regioisomers were found as products in platinum-catalyzed reactions. Low enantioselectivities, up to 7.5 and 27.5% *ee*, were obtained for 2-(4′-methoxyphenyl)-butanal in asymmetric hydroformylation of 1-(4′ methoxyphenyl)-propene by rhodium–DIOP catalyst and in the hydroformylation of 3-(4′-methoxyphenyl)-propene by platinum–tin(II) chloride–BDPP catalyst, respectively [64].

The new $[Rh_2(\mu\text{-BCOS})(COD)_2]_2$ ((+)-H_2BCOS = **28**) complex was tested as a catalyst precursor in the enantioselective hydroformylation of styrene. Enantiomeric excess up to 55% was achieved in the presence of BDPP (**29**) which reveals a slight cooperative effect between the dithiolate and the diphosphine ligand [65].



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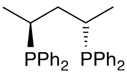

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Mono- and biphasic asymmetric hydroformylation of styrene with rhodium catalysts of the two enantiomers of NAPHOS (**30**) and its sulfonated derivatives was studied. Optical yields were found to be lower in two-phase hydroformylation compared with the conventional single-phase (organic solvent) technique [66].

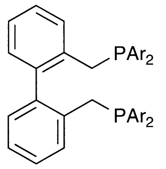
Rhodium complexes of aryl bis(diphenylphosphinomethyl)amino ligands $ArN(CH_2PPh_2)_2$ ($Ar = C_6H_5$, $p\text{-}CF_3C_6H_4$, $p\text{-}Me_2NC_6H_4$) were found to be active catalysts in the hydroformylation of 1-octene and 2-vinylnaphthalene [67].

Complexes of Pd, Ir, Rh, and Ni with a dendritic diphosphane were found to be useful as catalysts for hydroformylation [68].

The electronic effects of electron withdrawing aryl substituents on equatorial and apical diphosphines were studied. Diphosphines (**31**–**33**) designed to coordinate in diequatorial or in apical–equatorial positions were synthesized, and their effects on regioselectivity of rhodium-catalyzed 1-hexene hydroformylation were observed in benzene solution at 36 °C under 6 bar of $H_2:CO = 1:1$ using 0.2 mol% catalyst prepared from $Rh(CO)_2(acac)$ and diphosphine (Rh:diphosphine = 1:1). It was found that the electron withdrawing $-CF_3$ groups in **31** and **32** led to an increase in n-aldehyde regioselectivity in the rhodium-catalyzed hydroformylation. In **33**, however, the $-CF_3$ groups led to a decrease in n-aldehyde regioselectivity [69].

Bulky phosphabenzene-modified rhodium complexes were found to be highly efficient hydroformylation catalysts for internal and terminal olefins. Thus, the rhodium catalyst modified with *o*,*o*′-diphenyl substituted monophosphabenzene **34** showed 74 times higher activity than the standard PPh_3–rhodium catalyst for hydroformylation of cyclohexene at 90 °C in toluene at 20 bar initial total pressure of $CO:H_2 = 1:1$.

The same catalyst but in the hydroformylation of styrene at 25 °C showed four



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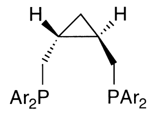

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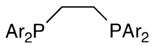

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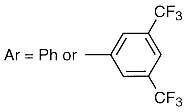

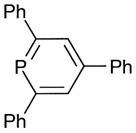

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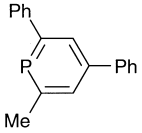
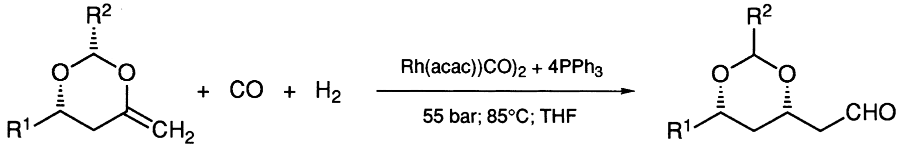


35

times higher activity than the standard PPh_3–rhodium catalyst leading to a branched:linear aldehyde ratio of 20:1 with 100% selectivity. A catalytically active phosphabenzene rhodium complex with ligand **35** was structurally characterized by X-ray crystallography [70].

Rhodium-catalyzed hydroformylation of 4-methylene-1,3-dioxanes (**36**) was found to proceed highly diastereoselectively and in good yield to produce **37** in 71–81% yield with >50:1 stereoselectivity [71].

See also refs. [72–75].



36 **37**

$R^1 = CHMe_2, H, Me; R^2 = CMe_3$

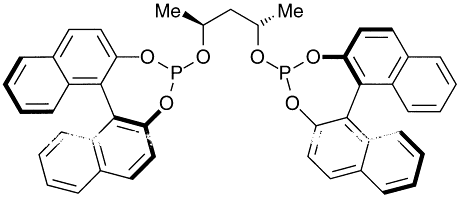
$R^1 = Me, PhCH_2OCH_2CH_2, Me_2C{=}CH(CH_2)_5; R^2 = Me$

1.1.3. Other metals as catalysts and bimetallic catalysts

Ruthenium carbonyl acetate complexes containing various 2,2′-bipyridines or 1,10-phenanthrolines ligands were tested as catalysts in the hydroformylation of 1-hexene in THF–water (30:5) solution at 150 °C and 100 bar H_2:CO = 1:1. The regioselectivity to n-heptanal varied between 67 and 86% [76].

Iron–rhodium mixed-metal nitrido-carbonyl clusters $[Fe_5RhN(CO)_{15}]^{2-}$ and $[Fe_4Rh_2N(CO)_{15}]^-$ were found to be moderately active catalysts for the hydroformylation of 1-pentene, but display low selectivity (35–65%) in n-hexanal and are demolished under catalytic conditions [76]. The heterobimetallic complex FeRh(μ-CO)(CO)$_3$[μ-P(^{t}Bu)$_2$](μ-dppm) was found to act as a catalyst precursor in the homogeneous hydroformylation of ethylene, but decomposes during the process [77,78].

Asymmetric hydroformylation of styrene using bis(phosphite)PtCl$_2$–SnCl$_2$ systems was found to give the branched aldehyde with high enantioselectivity. The highest enantioselectivity (91%) was obtained using **38** and its enantiomer as the chiral auxiliary at 17 °C in methylene chloride at a substrate/Pt ratio of 5000 [79].



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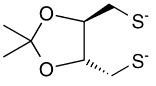
Platinum–dithiolato–SnCl$_2$ systems were found to be active in the hydroformylation of styrene. At 100 bar (CO:H$_2$ = 2:1) and 125 °C, [Pt(dithiolate)(P–P)]/SnCl$_2$ (Pt:Sn = 20:1) (dithiolate = DIOS (**39**), BINAS (**40**); P–P = dppp, dppb) systems provide aldehyde conversion up to 80%. Enantiomer excess of the 2-phenylpropanal product is 14% in the best case [80].



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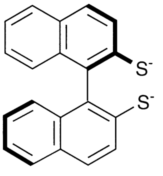

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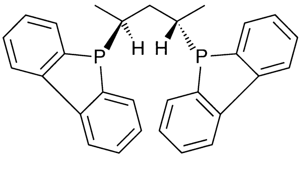
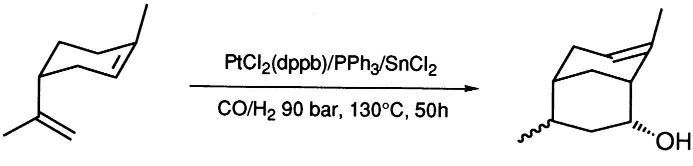
The SnCl$_2$ adducts *trans*-[PtCl(SnCl$_3$)(*S*,*S*-BDBPP)]$_n$, *cis*-PtCl(SnCl$_3$)-(*S*,*S*-BDBPP) and *cis*-PtCl(SnCl$_3$)(*S*,*S*-BDPP) (*S*,*S*-BDBPP = **41**, *S*,*S*-BDPP = **29**) were tested as catalysts in the asymmetric hydroformylation of *p*-isobutylstyrene. Up to 75% *ee* but only moderate yields to chiral 2-(4-isobutylphenyl)-2-propanal were observed [81].



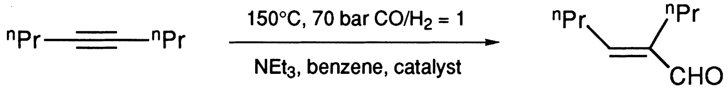
41

A convenient one-pot synthesis of **42** via platinum/tin-catalyzed hydroformylation/cyclization of limonene has been reported. Thus, limonene was converted in one step into two diastereomers of **42**, employing $PtCl_2(PPh_3)_2/PPh_3/SnCl_2$ and $PtCl_2(diphosphine)/PPh_3/SnCl_2$ systems as bifunctional catalysts (diphosphine = dppp and dppb). In the presence of the $PtCl_2(dppb)/PPh_3/SnCl_2$ system the selectivity for **42** reached the value of 82% at 95% conversion of limonene [82].

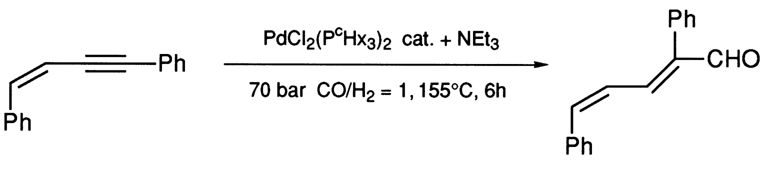


42

Selective hydroformylation of internal acetylenes has been achieved by using $PdCl_2(P^cHx_3)_2$ as the catalyst. The use of the $PdCl_2(P^cHx_3)_2–Co_2(CO)_8$ bimetallic catalyst system significantly improves the catalytic activity without lowering the selectivity. E.g.: hydroformylation of 4-octyne catalyzed by 2 mol% $PdCl_2(P^cHx_3)_2$ results in 84% conversion of 4-octyne and 83% yield of 2-propyl-hex-2-enal (95% *E*) in 6 h. Using 2 mol% of $PdCl_2(P^cHx_3)_2 + Co_2(CO)_8$ as the catalyst gives 100% conversion and 95% yield, respectively, in 1 h reaction time.

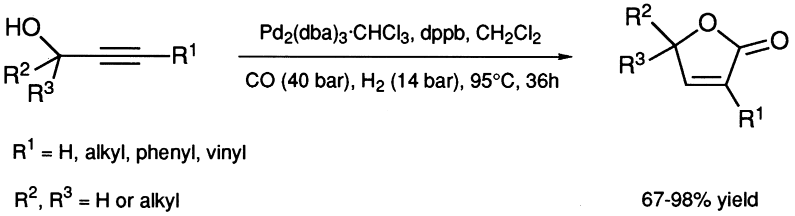


The $PdCl_2(P^cHx_3)_2$ and $PdCl_2(P^cHx_3)_2 + Co_2(CO)_8$ catalyst was found to be chemoselective for the hydroformylation of the carbon–carbon triple bond. Thus the hydroformylation of (*Z*)-1,4-diphenyl-1-buten-3-yne with the $PdCl_2(P^cHx_3)_2$ catalyst (155 °C, 6 h) gives (2*E*,4*Z*)-2,5-diphenyl-2,4-pentadienal as the exclusive carbonylation product in ca. 80% conversion and 39% isolated yield [83].



The effect of triflate additives in platinum-catalyzed enantioselective hydroformylation of styrene was investigated. It was found that the high enantiomeric excess of 2-phenyl-propanal using the optically active Pt–bdpp system was decreased in the presence of triflate anion. The activity of the catalyst was reduced but the regioselectivity towards the 2-phenyl-propanal was increased by the addition of silver triflate [84].

Substituted alkynols were found to undergo direct carbonylation to the corresponding substituted 2(5*H*)-furanones in 67–98% yield using $Pd_2(dba)_3 \cdot CHCl_3$ (4 mol%) (dba = dibenzylideneacetone) and 1,4-bis(diphenylphosphino)butane (8 mol%) in dichloromethane under an atmosphere of CO (40 bar) and H_2 (14 bar) at 95 °C for 36 h. 1,3-Bis(diphenylphosphino)propane, PPh_3 and P^cHx_3 were found to be equally effective for the reaction [85].
See also ref. [64].



1.2. Heterogeneous systems

1.2.1. Supported complexes

In situ infrared spectroscopy coupled with dynamic and steady-state isotopic transient kinetic analysis was used to examine the reaction pathway, reactivity of absorbates, and nature of sites for the $CO/H_2/C_2H_4$ reaction on $Mn–Rh/SiO_2$. Dynamic infrared study reveals that rhodium(0) sites which chemisorb linear CO actively catalyze CO insertion. Infrared studies by pulse injection of D_2 and ^{13}CO reveal that multiple pathways for hydrogenation take place simultaneously with a wide distribution of the reactivity of absorbed deuterium or hydrogen in contrast to the narrow distribution of reactivity of absorbed CO for CO insertion [86,87].

The catalytic properties of oxide-supported triruthenium ketenylidene clusters were investigated. In hydroformylation of ethylene, MgO-supported triruthenium ketenylidene species showed high activity and selectivity for formation of oxygenates, while the $SiO_2–Al_2O_3$-supported triruthenium ketenylidene cluster exhibited a high activity for the formation of ethane [88].

Hydroformylation of ethylene and the hydrogenation of carbon monoxide were studied over a cobalt-based catalyst derived from reaction of $Co_2(CO)_8$ with ZnO, MgO and La_2O_3 supports. At 160 °C a similar activity sequence was found for both reactions; i.e. $Co/ZnO > Co/La_2O_3 > Co/MgO$. In the carbon monoxide hydrogenation the selectivity towards $C_1–C_3$ alcohol mixtures was found to be near 100% at 160 °C for a conversion of 6% over the Co/ZnO catalyst. This catalyst showed oxo selectivity higher than 98% in the hydroformylation of ethylene. These confirm the deep analogy between hydroformylation and carbon monoxide hydrogenation into alcohols. It is suggested that the active site for the step that is common to both reactions is related to the surface homonuclear $Co^{2+}/[Co(CO)_4]^-$ ion-pairing species [89,90].

Atmospheric ethylene hydroformylation results have shown that the

$RhCo_3(CO)_{12}$-derived SiO_2-supported catalyst has high activity and stability at 150 °C for the formation of propanal and n-propanol. The bimetallic $RhCo_3$ framework was found to be preserved intact on the surface after thermal treatments of $RhCo_3(CO)_{12}/SiO_2$ at 350 °C under vacuum, dihydrogen, and dioxygen (or air), and the initial bimetallic carbonyl cluster regenerates under a carbon monoxide atmosphere [91–96].

Doped cobalt on silica-supported rhodium catalyst was found to result in a strong enhancement of catalytic activity in propylene hydroformylation [97].

Hydroformylations of mono and multiple unsaturated fatty substances using heterogenized cobalt carbonyl and rhodium carbonyl catalysts were studied. The cobalt-catalyzed reaction gives with polyunsaturated fatty substances almost only products with monofunctionalized fatty acid chains. The rhodium-catalyzed reaction gives with linoleic and linolenic acid compounds mixtures of mono- and diformyl derivatives [98,99].

Supported aqueous-phase hydroformylation of 1-alkenes was tested using rhodium, platinum–tin(II), and cobalt complexes containing hexyl-bis(sodium-*m*-sulfonatophenyl)phosphine, and tris[ω-(sodium-*p*-sulfonatophenyl)-(methylene)$_n$-phosphines] ($n=1$, 2, and 3) formed in situ. With the exception of the cobalt system, the supported aqueous-phase catalytic systems show similar selectivity as the corresponding non-aqueous homogeneous catalysts. The cobalt system gives lower linear selectivities than the analogous homogeneous system. Asymmetric hydroformylation of styrene using the chiral supported aqueous-phase catalyst $PtCl_2[((S,S)\text{-BDPP-}((p\text{-}NMe_3)(BF_4))_4)] + SnCl_2$ on controlled-pore glass showed low activity and low enantiomeric excess of the branched aldehyde [100].

Aluminium phosphate molecular sieve VPI-5 was impregnated with $ClRh(PPh_3)_3$ and $HRh(CO)(PPh_3)_3$ and the resulting material was evaluated as catalysts for hydrogenation and hydroformylation of the water soluble alkene, sodium 4-styrenesulfonate, in aqueous media. Hydrogenation reactions at 50 °C and 28 bar gave good yield of sodium 4-ethylbenzenesulfonate using the $ClRh(PPh_3)_3$/VPI-5 catalyst. Hydroformylation, at 70–90 °C using the catalysts, gave low yields of the expected aldehydes together with substantial amounts of poly(sodium 4-styrenesulfonate) [101–103].

Thiourea-functionalized siloxane materials were used for the anchoring of rhodium(I) species giving supported complexes that were found to be very active and recoverable catalysts for the hydroformylation of styrene at 80 °C and 60 bar $CO:H_2=1:1$ [104].

The hydroformylation of isobutene in the presence of rhodium carbonyl catalysts immobilized on polymeric pyrrolidinopyridines was studied. It was found that the thermostable polymeric catalyst has high activity in the hydroformylation of isobutene under the conditions when the activity of conventional homogeneous catalysts is low [105,106]. The catalyst system composed of $Rh(acac)(CO)_2$ and polyorganosiloxanes was found to be highly active and stable for hydroformylation of 1-hexene. The effects of the nature of the polyorganosiloxane, the ratio of oligomers, and the oligomer:rhodium ratio in the catalyst on the catalytic properties of the system were investigated [107,108]. Polymer-supported rhodium(I) complex from $Rh(acac)(CO)_2$ and $MeCH_2(CH_2CH_2)_nP(OPh)_2$ was evaluated as a hydroformylation catalyst for 1-dodecene. Optimum tridecanal:2-methyldodecanal selectivity of 4 was observed when the reaction was conducted in the presence of excess triphenylphosphite with $P(OPh)_3$:Rh = 40. Excess $MeCH_2(CH_2CH_2)_nP(OPh)_2$ also improved the normal:iso selectivity [72,73]. Three types of immobilized rhodium complex on polymeric supports, including styrene–divinyl benzene copolymers, inorganic compounds functionalized with phosphines or amines, and vinylpyridine copolymer crosslinked with divinylbenzene were prepared and their properties, activities, selectivities and the normal/iso ratio were studied for hydroformylation of propylene and 1-octene at 120–130 °C and 30–90 bar $CO:H_2 = 1:1$ [109,110].

Supported mixed bidentate rhodium and iridium complexes derived from phosphonate–phosphanes were studied for methanol carbonylation and hydroformylation of ethylene and propylene. It was found that phosphonate–phosphane ligands suppress the undesired ethane formation in ethylene hydroformylation. Excellent rhodium catalysts for vapor-phase carbonylations were obtained, when rhodium phosphane complexes were anchored in lamellar zirconium phosphonate structures with mixed phosphonate anions. These catalysts were found to be several times more active than rhodium supported on silica or on activated carbon, and show a superior stability, and produce butyraldehydes with up to 98% chemoselectivity in the vapor-phase hydroformylation of propylene [111,112].

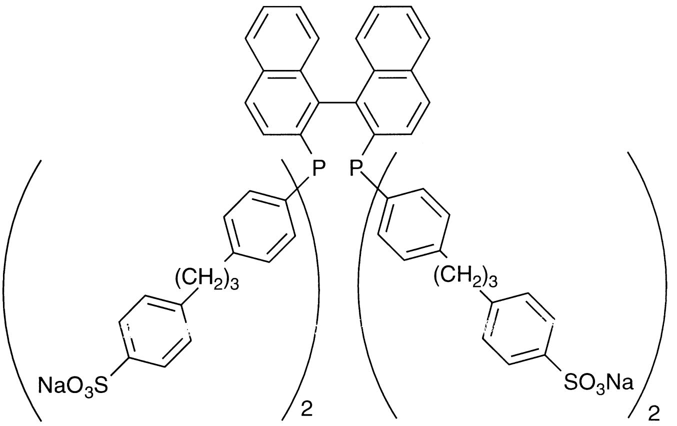
Structure and catalytic activity of $Ir_4(CO)_{12}$ bound to tris(hydroxymethyl)phosphine grafted silica was studied. Evacuation at 100 °C gave an active catalyst for hydroformylation of ethene. The ethene hydroformylation proceed on the evacuated catalyst at lower temperatures compared with other conventional iridium catalysts [113].

1.2.2. Biphasic systems

A novel water-soluble rhodium-poly(enolate-co-vinyl alcohol-co-vinyl acetate) catalyst has been tested for the hydroformylation of olefins under biphasic reaction conditions. The average turnover frequency for the catalytic hydroformylation of 1-octene was found to be 5.49×10^{-5} kmol (kg Rh s)$^{-1}$ at 90 °C, and that of 1-dodecene 2.36×10^{-4} kmol (kg Rh s)$^{-1}$ at 60 °C. Excellent selectivity for the preparation of branched-chain aldehydes was found for styrene and its derivatives, albeit at low conversion [114].

Two-phase hydroformylation of 1-octene with an in situ rhodium catalyst of the water-soluble phosphines **43** and **44** was investigated. It was found that the rhodium catalyst with **44** offers both good activity under two-phase conditions and excellent selectivity (97% of 1-nonanal, at Rh/P ratio of 1/9 at 120 °C and 15 bar $CO:H_2 = 1:1$) [115].

The effect of pH on rate and regioselectivity of $RhCl(COD)_2$/TPPTS-catalyzed hydroformylation (TPPTS = trisodium salt of the trisulfonated triphenylphosphine) of 1-octene in a biphasic medium composed of water, ethanol, 1-octene and octane was studied. The rates were found to increase by two- to five-fold when the pH was changed from 7 to 10, and higher normal/iso aldehyde ratios were observed at



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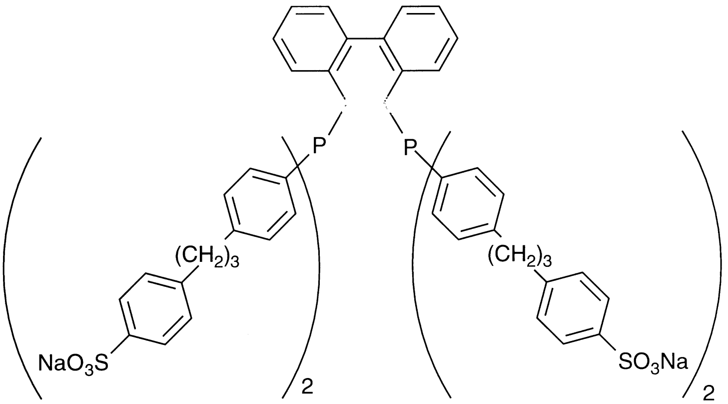

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pH 10. The influence of olefin, catalyst, H_2 and CO concentration on the rate and regioselectivity at both pH values was explored as well [116].

The selectivity of water-soluble catalytic systems based on $RhCl_3$ and polycation in the biphasic hydroformylation of 1-hexene was studied. It was found that the introduction of a long chain alkyl group into the polycation or the use of a higher fatty acid counterion resulted in the increase of the selectivity to n-aldehyde up to 60% at $pH > 7$ [117,118].

Quaternary ammonium salts of sulfonated tertiary phosphines were used as catalyst components in rhodium-catalyzed olefin hydroformylation. A special advantage of these catalyst systems is the possibility of metal recycling by using phase separation or membrane technique [119].

A new commercial process was developed for the production of n-valeric acid based on the low pressure HRh(CO)[P(*m*-sulfophenyl-sodium)$_3$]$_3$-catalyzed hydroformylation of 1-butene rich feedstock in a two-phase system and subsequent oxidation. In the low pressure hydroformylation of 1-butene a 95:5 ratio of n-valeraldehyde and 2-methyl-butyraldehyde was achieved [120]. Membrane separation technology was successfully used for removing decomposition products and recycling the rhodium complex hydroformylation catalyst from the oxo products in two-phase systems and in one-phase systems. In a three-month pilot plant trial 99% rhodium retention and 98% ligand retention was achieved [74].

A series of novel water-soluble polyether-substituted triphenylphosphines was prepared by ethoxylation of mono-, di-, and tri-*p*-hydroxytriphenylphosphines and their rhodium complexes were tested as catalyst in the thermoregulated two-phase hydroformylation of 1-hexene, 1-octene, and 1-dodecene. The catalysts exhibit very good catalytic properties with the conversion up to 93% and the selectivity for aldehyde about 85% at 100 °C and 50 bar $CO:H_2=1:1$ in a water–toluene system. At room temperature, almost all catalyst is in the aqueous phase. On heating to 100 °C the catalyst transfers into the toluene phase where it transforms olefins into aldehydes. After hydroformylation is complete and the system is cooled to room temperature, the catalyst returns to water [121]. The biphasic hydroformylation of styrene was studied using ethoxylated tri(*p*-hydroxyphenyl)phosphine rhodium complex as the catalyst. The results showed that the reaction took place mainly in the organic phase at 90 °C and 60 bar $CO:H_2=1:1$ in toluene leading to 98% conversion of styrene, 94.4% yield of aldehyde with a 1.4 iso/normal ratio [122,123]. Hydroformylation of 1-dodecene in aqueous–organic media using the system phosphine–functionalized polyethylene oxide + Rh(acac)(CO)$_2$ was studied. Optimal conditions were found to be P:Rh = 15 and 50 °C [124,125].

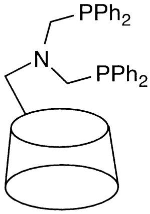
The selectivity for EtCHMeCHO in the phosphine-modified RhCl$_3$–polyelectrolyte olefin hydroformylation system under two-phase conditions was found to decrease in order of ligands: erythritol phosphite $\sim$ P(OPh)$_3$ $>$ Ph$_3$P $\gg$ Bu$_3$P. Optimal results with mixed 2-butenes were obtained using erythritol phosphite ligand in 2:1 = P:Rh ratio and poly(ethyleneimine) as the polyelectrolyte [126,127].

Rhodium complexes with β-cyclodextrin-modified diphosphanes **45–48** as ligands were found to be extremely active and selective when employed in the hydroformylation of 1-octene and *E*-3-hexene in a two-phase system.

Thus, in the hydroformylation of 1-octene in the two-phase system water (30% DMF)/olefin with 0.03 mol% of the catalyst **46**/[Rh(COD)]BF$_4$ at 80 °C and 100 bar, quantitative conversion was achieved in 18 h (turnover number 3172), with 76% regioselectivity in favor of the linear aldehyde product [128].

A new phosphine-free two-phase cobalt catalyst for hydroformylation of 1-hexene (120 °C, 70 bar $CO:H_2=1:1$, 3 h) has been developed from [tris(tricarbonylcobalto)-methylidine]trichlorosilane and poly(ethylene glycol) 400 ($n=9$) [129,130].

Non-aqueous room-temperature organic–inorganic ionic liquids of the BMI$^+$A$^-$



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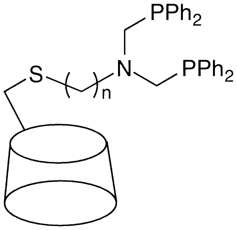


46 n = 2

47 n = 3

48 n = 4

type (BMI$^+$ = 1-butyl-3-methylimidazolium, A$^-$ = $Al_2Cl_7^-$, $AlCl_4^-$, BF_4^-, PF_6^-, and SbF_6^-) were used as a new class of solvents for two-phase catalytic organic reactions such as the hydroformylation of olefins [131,132].

A new method for the hydroformylation of ethylene using a gas cell composed of C_2H_4, CO, cathode/H_3PO_4 aq./anode (Pt black), H_2 was examined at ~100 °C and atmospheric pressure. Among many cathode electrocatalysts tested, H_2PtCl_6 showed the highest selectivity and high activity for the formation of propionaldehyde [133,134]. See also ref. [66].

1.3. Coordination chemistry related to hydroformylation

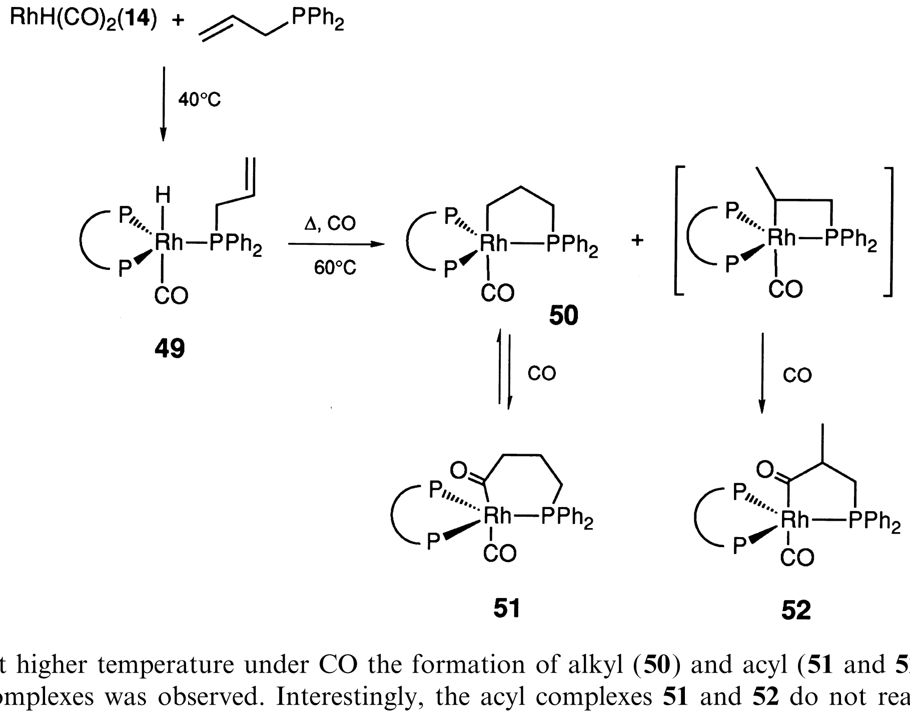
The behavior of n-propyl- and isopropylcobalt tricarbonyl tributylphosphine under hydroformylation conditions was tested. It was found that at 120–180 °C, $P(CO) = 5$ bar, $P(H_2) = 50$ bar the expected isomeric alcohols were obtained with a selectivity higher than 95% in the presence or absence of an excess of an olefin (1-hexene) or tributylphosphine [135].

Some heterobimetallic acyl and m-acyl-rhodium complexes were isolated from reactions of the phosphido-bridged complexes $(OC)_4M(\mu\text{-}PPh_2)RhH(CO)(PPh_3)$ (M = Cr, Mo, W) with the phosphidoalkenes $Ph_2P(CH_2)_nCH{=}CH_2$ ($n = 1, 2, 3$) and their potential role as intermediates in the catalytic hydroformylation of the parent phosphines investigated [136,137].

The potential energy profile for the full cycle of olefin hydroformylation catalyzed by $RhH(CO)_2(PH_3)_2$, consisting of olefin coordination and insertion, carbon monoxide insertion, dihydrogen oxidative addition, and aldehyde reductive elimination, as well as ligand coordination and dissociation, has been investigated using an ab initio molecular orbital method. Structures of nearly all isomers of intermediates and transition states involved in each step have been determined mainly at the Hartree–Fock level, and the potential energy profile was calculated at MP2 and MP4 levels. The preference of trigonal-bipyramidal intermediates and transition states was found [75]. The stereochemistry of $Rh(CO)(PH_3)_3R$ (R = H, C_3H_6) was investigated in a quantum chemical study. Calculations have shown that in favor of total energy the rhodium atom intended to move from the plane of the three phosphor atoms towards the carbon monoxide, and the olefin intended to attack and coordinate to the rhodium atom from opposite of carbon monoxide [138,139].

The ligand dissociation in rhodium-catalyzed hydroformylation has been investigated in a theoretical study. The equilibrium structures of rhodium complexes $HRh(CO)_n(PR_3)_{4-n}$ and $HRh(CO)_n(PR_3)_{3-n}$ with $n = 1$–3 and R = H were calculated using density functional theory with both local and gradient-corrected functionals. The ligand dissociation energies derived from single-point CCSD(T) calculations revealed that MP2 strongly overestimates bond strengths for these systems. The density function theory calculations using gradient-corrected functionals yielded values very close to the CCSD(T) energies. Comparison with experimental results for PPh_3 complexes shows that the phosphine dissociation energies are calculated too low when PH_3 serves as the model phosphine. When PMe_3 is used instead, the dissociation energy is 7.2 kcal/mol larger than for PH_3 ($n = 1$) [140].

Intermediates in the bulky diphosphite (**14**) modified rhodium-catalyzed hydroformylation of allyldiphenylphosphine were studied using NMR spectroscopy. In the reaction of equimolar amounts of $RhH(CO)_2$(**14**) and allyldiphenylphosphine in benzene at 40 °C the formation of **49** was observed in which all three phosphorus ligands are coordinated equatorially.



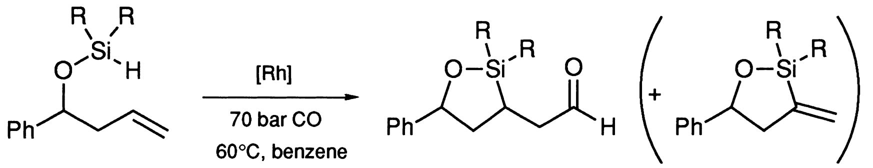
At higher temperature under CO the formation of alkyl (**50**) and acyl (**51** and **52**) complexes was observed. Interestingly, the acyl complexes **51** and **52** do not react with H_2 to the corresponding aldehydes. This might be a result of the too stable coordination of the three phosphorus ligands in the equatorial positions, thereby preventing the necessary coordination of H_2 in one of those positions preceding the aldehyde formation [141].

Under the mild conditions of 120 or 150 °C and 27 bar CO pressure, $RhCl(CO)(PEt_3)_2$ was found to be a better precursor than $[Rh(CO)_2Cl]_2$ for the catalytic methanol carbonylation to acetic acid leading to higher rates. Intermediates in the catalytic cycle were identified and characterized [142]. See also ref. [57].

2. Hydroformylation related reactions of CO

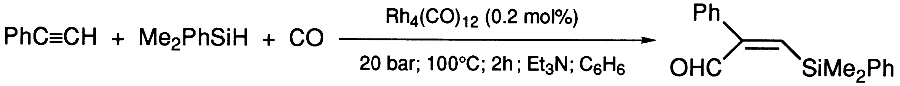
2.1. Silylformylation, hydrocarboxylation, alkoxycarbonylation and amidocarbonylation

The intramolecular silylformylation of β-siloxy alkenes has been achieved at 60 °C and 70 bar in the presence of $Rh(acac)(CO)_2$ as the catalyst [143].



R = Ph, ^{i}Pr

The simultaneous introduction of a trialkylsilyl group and a formyl group into a carbon–carbon triple bond to give 3-silyl-2-alkenal selectively has been found in the rhodium-catalyzed silylformylation [144]. E.g.:



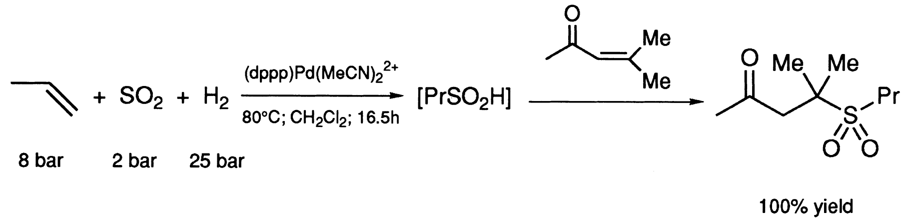
Z : *E* = 88 : 12

89% yield

A dissertation (227 pp.) dealing with rhodium-catalyzed silylformylations, hydrocarbonylations, and related reactions was reported [145,146].

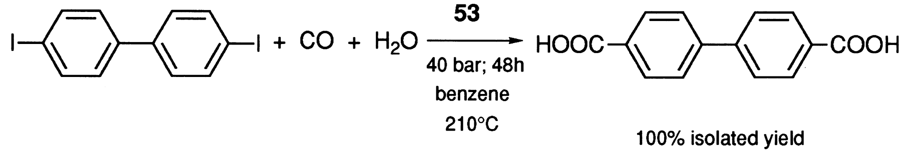
In analogy to hydroformylation, alkenes were found to react with sulfur dioxide and dihydrogen in the presence of cationic palladium(II) or platinum(II) complexes with chelating diphosphines as ligands as the catalyst to give sulfinic acids. Sulfinic acids are not stable under the reaction conditions but they can be trapped in situ by adding α,β-unsaturated carbonyl compounds to the reaction mixtures leading to γ-oxo sulfones in good yields [147]. E.g.:

In the palladium-catalyzed selective hydroxycarbonylation of higher α-olefins in biphasic medium, chemically modified β-cyclodextrins were found to be more efficient than co-solvents [148,149].



In the hydrocarboxylation of 4-methylstyrene at 100 °C and 45 bar CO using the homogeneous catalyst system of $PdCl_2$–$CuCl_2$–PPh_3 in water in the presence of hydrochloric acid under the optimized reaction conditions, 100% conversion and 93% selectivity to the branched acid were obtained [150].

The binuclear rhodium complex $[(Ph_3P)_4Rh_2(\mu\text{-}OH)_2]\cdot 2C_6H_6$ (**53**) was found to be an effective catalyst for the carbonylation of aryl halides to acids. Thus, the treatment of iodobenzene and water in the presence of 0.5 mol% of **53** in benzene at 210 °C and 40 bar carbon monoxide for 16 h affords benzoic acid in 99% isolated yield. Iodobenzenes having a *m*-methyl, *p*-methyl, *m*-chloro, *p*-chloro, *m*-bromo, *p*-bromo group or 1-iodonaphthalene show high reactivities to give the corresponding acids in good to excellent yields. However, *m*-iodoanisole and *p*-iodoanisole give poor results, 26% and 5% yields of the corresponding acids, respectively. This rhodium-catalyzed carbonylation was found to be applicable to the synthesis of diacids as well [151]. E.g.:



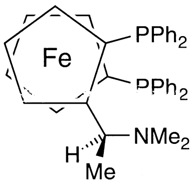
Cationic palladium complexes were found to be useful catalyst precursors for the hydroesterification of styrene or 4-isobutylstyrene under mild conditions to afford the branched ester regioselectively. E.g.:

$$\mathrm{PhCH{=}CH_2 + CO + MeOH} \xrightarrow[\substack{\mathrm{MeC_6H_4SO_3H} \\ \text{r. t., 20 bar, 20h}}]{\mathrm{Pd(OAc)_2,\ PPh_3,}} \mathrm{PhCHMeCOOMe + Ph(CH_2)_2COOMe}$$

$$\underbrace{93 \qquad : \qquad 7}_{\text{95\% yield}}$$

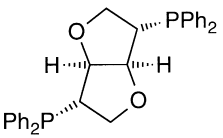
Relatively high asymmetric induction (86% optical yield) was achieved in the hydroesterification of styrene by the use of a ferrocene-containing chiral aminophosphine **54** instead of PPh_3, although the product yield (17%) and the selectivity to the branched ester (44%) were low [152].

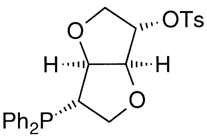
Asymmetric induction up to 99% and good regioselectivities have been obtained in the hydroesterification of styrene with carbon monoxide and methanol at 80 °C



54

and 50 bar pressure in the presence of $PdCl_2$–$CuCl_2$ and chiral phosphines such as **55** and **56** [153].





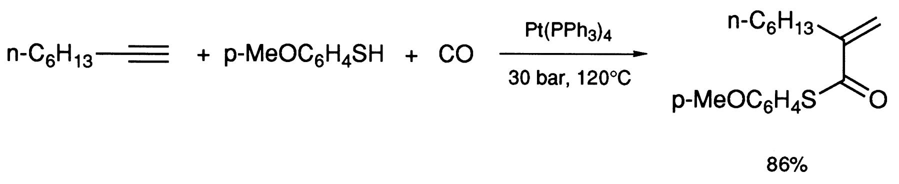
55 **56**

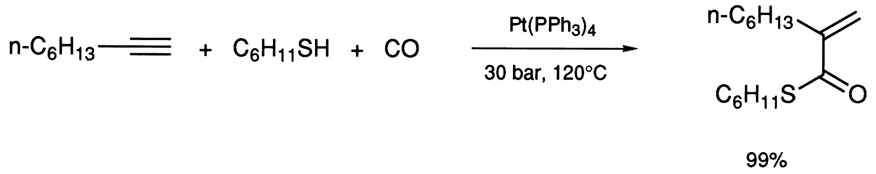
A computer-aided mechanism elucidation of palladium complex-catalyzed acetylene hydrocarboxylation to acrylic acid was developed based on a novel union of empirical and formal methods. The pathways reported by the programs were categorized as hydride, hydroxycarbonyl (alcoholate-like), and metallocyclic. The programs accommodate prior knowledge of what can or what cannot happen [154].

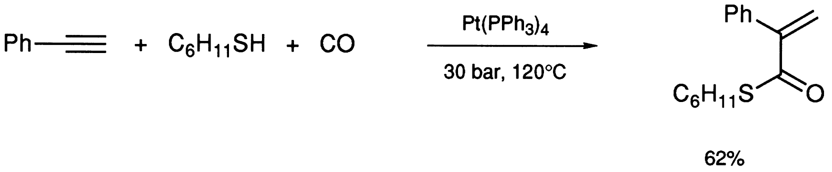
In a new two-phase system, water-soluble palladium complex of trisulfonated triphenylphosphine as catalyst and a Brønsted acid as promoter were used to transform alkenes into carboxylic acids under carbon monoxide [155,156]. Turnover frequencies higher than 2500 h^{-1} have been achieved in the biphasic hydrocarboxylation of propene catalyzed by water-soluble palladium–$P(C_6H_4\text{-}m\text{-}SO_3Na)_3$ complexes. The hydrocarboxylation of 4-isobutylstyrene and styrene in a two-phase system is also reported [157,158]. The kinetics and mechanism of styrene hydrocarboxylation catalyzed by the $SnCl_2$-modified $PdCl_2(PPh_3)_2$ complex and the effect of $SnCl_2$ additives on the regioselectivity were studied. It was found that the addition of $SnCl_2$ in an equimolar amount to $PdCl_2(PPh_3)_2$ increases the selectivity to 3-phenylpropionic acid from 30 to 70% [159,160].

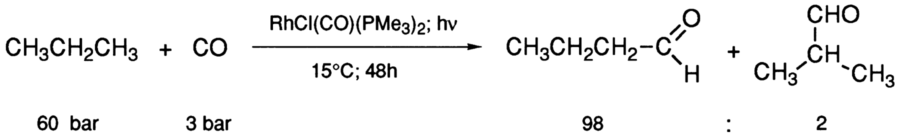
The hydrothiocarboxylation of acetylenes with thiols and carbon monoxide in acetonitrile was achieved in good to excellent yields at 120 °C and 30 bar CO pressure in the presence of $Pt(PPh_3)_4$ (3 mol%) as the catalyst [161]. E.g.:

Direct carbonylation of liquefied propane to produce n-butanal with high regioselectivity was achieved by irradiation using a high-pressure mercury lamp and $RhCl(CO)(PMe_3)_2$ as the catalyst at 15 °C. Turnovers of 20.3 were observed for n-butanal and 0.36 for isobutanal [162]. See also refs. [18,111,112].





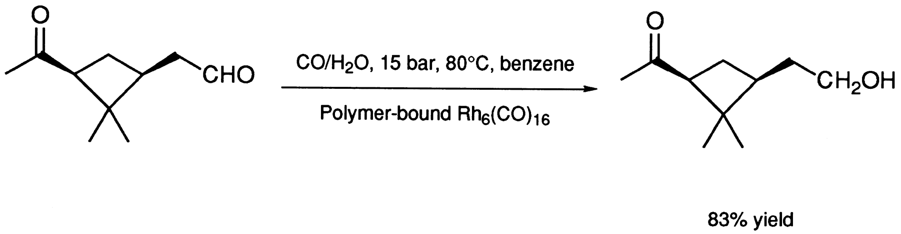




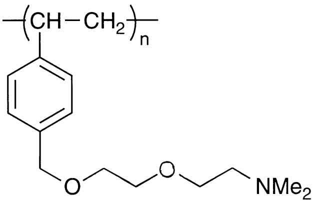
2.2. Water–gas shift reaction and reduction with CO or CO+H_2O

Homogeneous catalysis of the water–gas shift reaction by $RhCl_3 \cdot 3H_2O$ in aqueous piperidine (2/8 v/v) was found to result in about 19 mol H_2/mol rhodium/day for [Rh] = 10 mM at 100 °C and 0.9 bar CO pressure [163,164].

The amino-substituted polymer **57** combined with $Rh_6(CO)_{16}$ was found to be an active catalyst for the highly chemoselective reduction of the aldehyde functional group under water–gas shift conditions at 80 °C and 10–15 bar pressure of carbon monoxide. E.g.:



In the presence of acetophenone, benzaldehyde is reduced to benzyl alcohol in 95% yield without formation of 1-phenylethanol from acetophenone.

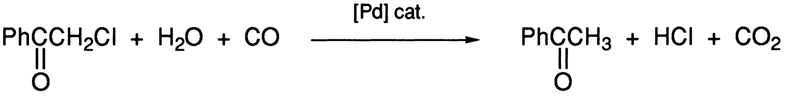


57

The recovered polymeric rhodium catalyst gave 93% yield of benzyl alcohol without appreciable loss of its activity under the same conditions as in the case of a fresh catalyst [165].

Catalytic reduction of amine oxides and organoselenium oxides by carbon monoxide has been achieved by using rhodium(I) carbonyls such as $RhCl(CO)(PR_3)_2$ (R = Me, Ph) and $IrCl(CO)_2(PPh_3)_2$ as the catalyst precursors. On the other hand, $PtCl_2(CO)(AsPh_3)$ was found to act as a good catalyst precursor for deoxygenation of arsine oxide by carbon monoxide [166].

$PdCl_2(PPh_3)_2$, in combination with a large amount of triphenylphosphine, was found to be an excellent catalyst precursor for the hydrodehalogenation of α-chloroacetophenone to acetophenone by hydrogen transfer from the water–carbon monoxide system. At 50–70 °C, 40–80 bar CO, substrate/Pd/P = 2000/1/50, H_2O/substrate = 8–12/1, 70–80% yield was found using ethanol or dioxane as a solvent [167].



$$PhC(=O)CH_2Cl + H_2O + CO \xrightarrow{[Pd]\ cat.} PhC(=O)CH_3 + HCl + CO_2$$

Mechanistic aspects of the reductive carbonylation of nitrobenzene catalyzed by the system $PdCl_2$–Keggin heteropolyanion to methyl phenylcarbamate were investigated using deuterated nitrobenzene as substrate. Results obtained in the presence of aniline, but in the absence of methanol, indicate that the reaction follows at least three different pathways. Aniline was found to be an intermediate in two of the possible pathways [168]. The binuclear rhodium complex $[(Ph_3P)_4Rh_2(\mu\text{-}OH)_2]\cdot 2C_6H_6$ was found to be an effective catalyst for the reductive carbonylation of nitrobenzene and a variety of nitroarenes to the corresponding carbamate esters. Thus, the treatment of nitrobenzene and methanol in the presence of a catalytic amount (0.5 mol%) of $[(Ph_3P)_4Rh_2(\mu\text{-}OH)_2]\cdot 2C_6H_6$ and 2,2′-bipyridyl in dry benzene at 180 °C under 69 bar of carbon monoxide for 16 h affords methyl *N*-phenylcarbamate selectively in 94% isolated yield. Electron withdrawing groups at the para-position enhance the reactivity of the substrate [169]. Methyl *N*-phenylcarbamate was synthesized in up to 88% yield by reductive carbonylation of nitrobenzene using homogeneous catalytic systems based on palladium and silver salts, 1,10-phenanthroline and *p*-toluenesulfonic acid. Copper(II) and mercury(II) acetates as co-catalysts in palladium-based bimetallic systems gave similar results [170]. See also ref. [18].

2.3. Reduction of CO and CO_2

Hydrogenation of carbon dioxide on the cathodized tungsten trioxide/polyaniline/polyvinylsulfate-modified electrode in aqueous solution was studied. It was found that the prolonged potentiostatic reduction of carbon dioxide leads to the formation of lactic acid, formic acid, ethanol and methanol under low overpotential [171].

Photoreduction of hydrogen carbonate to methane was achieved in an aqueous dimethyl sulfoxide solution using the catalyst system trisodium trisulfonatophthalocyaninzincate(II), 1,1′-dimethyl-4,4′-bipyridinium dichloride, and ruthenium colloid upon irradiation with visible light. The optimum pH for methane evolution was found to be 6.6 [172].

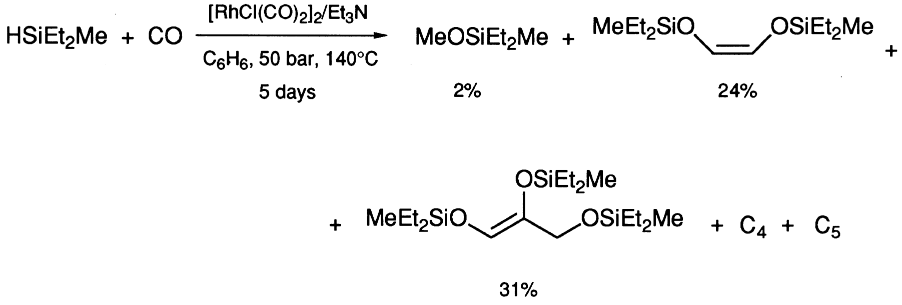
The very efficient hydrogenation of carbon dioxide was found to be catalyzed by soluble ruthenium complexes at 140–180 °C to obtain carbon monoxide and ethylene glycol in good yields with carbon dioxide conversions of 70%. The suggested reaction mechanism includes the insertion of CO_2 into ethylene oxide to form ethylene carbonate in the first step, followed by its hydrogenation [173,174].

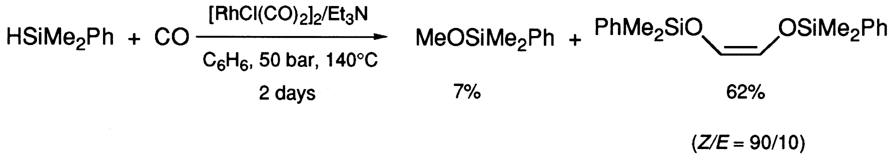
Complexes of the type $RuCl_2L_2$ ($L = Ph_2P(CH_2)_nPPh_2$, $n = 1–3$, $Me_2P(CH_2)_2PMe_2$) were found to be highly active and selective catalysts for the synthesis of formic acid derivatives from carbon dioxide, dihydrogen and dimethylamine or methanol–trimethylamine, respectively, without any additional solvent, affording at 100 °C with $RuCl_2(dppe)_2$ an extremely high turnover frequency of 360 000 h^{-1} in *N*,*N*-dimethylformamide synthesis and 830 h^{-1} in methyl formate synthesis [175].

The cationic bis(chelate) complex $[Rh(^cHx_2PCH_2CH_2OCH_3)_2]^+BPh_4^-$ was found to catalyze the hydrogenation of carbon dioxide to formic acid with turnover numbers of up to 1000 within 7 h in methanol solution at 55 °C and $P(CO_2) = 25$ bar and $P(H_2) = 50$ bar [176].

A unique molecular modeling approach was developed to define the accessible molecular surface of the rhodium center within the flexible $(P_2)Rh$ fragment of $(P_2)Rh(hfacac)$ (P_2 = a variety of chelating diphosphine ligands, hfacac = hexafluoroacetylacetonate). The potential of this model for application in homogeneous catalysis was exemplified using $(P_2)Rh(hfacac)$ as catalysts in a test reaction, the hydrogenation of carbon dioxide to formic acid. Complexes $(P_2)Rh(hfacac)$ are the most active catalyst precursors for this process in organic solvents known to date [177,178]. A theoretical and kinetic study has been made of the mechanistic aspects of the rhodium-catalyzed hydrogenation of carbon dioxide to formic acid. The mechanism of the reaction was investigated by initial rate measurements using the complex (dppp)Rh(hfacac) as a catalyst precursor in $DMSO/NEt_3$ and by ab initio calculations using *cis*-$(PH_3)_2Rh$ as a model fragment for the catalytically active site. The kinetic data were found to be consistent with a mechanism that involves rate limiting product formation by liberation of formic acid from an intermediate that is formed via two reversible reactions of the actual catalytically active species first with CO_2 and then with H_2. The calculations provide a theoretical analysis of the full catalytic cycle of CO_2 hydrogenation. The results suggest σ-bond metathesis as an alternative low energy pathway to a classical oxidative addition/reductive elimination sequence for the reaction of the formate intermediate with dihydrogen [179].

The properties of cluster-derived cobalt–ruthenium catalysts supported on silica were studied in CO hydrogenation. Catalysts prepared by the reflux method were found to show a higher activity per gram metal than do impregnated catalysts [180]. Reductive oligomerization of carbon monoxide has been observed in the reaction with hydrosilanes catalyzed by rhodium(I) complex at 140 °C [181].





See also refs. [89,90].

3. Reviews

(1) Hydroformylation (oxo synthesis, Roelen reaction). A review with 271 references [182,183].

(2) Organometallic homogeneous catalysis — Quo vadis? A review among others about hydroformylation with more than 133 references [184].

(3) Reactions of synthesis gas. A review with many references of the use of synthesis gas in manufacturing environmentally clean fuels and chemicals from Fischer–Tropsch synthesis, olefin hydroformylation, and carbonylation [185,186].

(4) Design of heterogeneous catalytic systems. New cement-containing catalysts.

A review with no references. Reaction mechanisms occurring during formation of cement-containing catalysts, physical and mechanical properties of the catalyst, and their use as hydrogenation, hydrorefining, hydroformylation and water–gas shift reaction catalysts are discussed [187,188].

(5) Current improvements in the synthesis of pharmaceuticals by the hydroformylation reaction. Part II. A review with 102 references [189,190].

(6) From metal carbonyls to fine chemical syntheses. A review with 17 references on selective homogeneous catalytic syntheses using in situ prepared rhodium phosphine catalysts. These catalysts were found to be useful for selective hydroformylation of functionalized substrates such as unsaturated carboxylic acids, tropenes, and steroids [191,192].

(7) Ruthenium complex-catalyzed carbonylation reactions. A review with two references on the carbonylation of allyl compounds and the hydroformylation of olefins [193,194].

(8) Application of phosphine ligands to hydroformylation of olefins. A review with 45 references [195,196].

(9) Evolution and significance of molecular design concept in the development of stereo-selective transition-metal complex catalysts. A review with 45 references among others about hydroformylation of α-olefins [197,198].

(10) Recent developments in aqueous organometallic chemistry and catalysis. A review about new water-soluble ligands and their catalytic application among others in aqueous biphasic hydroformylation with 114 references [199].

(11) Homogeneous catalysis in water: industrial perspective. A review with 40 references of recent advances in water-soluble organometallic homogeneous catalysis among others in hydroformylation of propene and higher olefins [200,201].

(12) Industrial aspects of aqueous catalysis. Hydroformylation. A review with 58 references [202].

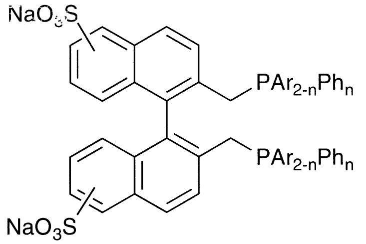
(13) Two-phase catalysis in non-aqueous ionic liquids. A review with 10 references on room temperature molten salts containing quaternary ammonium cations and anions as effective solvents for organometallic-catalyzed hydrogenation, hydroformylation, dimerization and metathesis reactions [203,204].

(14) Progress of catalysis of water-soluble transition metal complexes. A review with 35 references on water-soluble transition metal complexes and their catalysis on hydroformylation of alkenes and hydrogenation of unsaturated compound [205,206].

(15) BINAS: A new ligand with outstanding properties in the hydroformylation of propylene. A review on preparation and pilot plant application in biphasic propylene hydroformylation with >13 references [207].

(16) Water–gas shift reaction. A review with 20 references on topics of mechanism, applications, Arco ethylurethane process, and catalytic implications and perspectives [208,209].

(17) Other carbonylations. A review with 55 references. Hydrocarboxylation of alkenes, hydroesterification, dicarboxylation and other oxidative carbon-



(Ar = m-C$_6$H$_4$SO$_3$Na)

BINAS

ylations of alkenes, carbonylation of alkenes, and radical carbonylation, as well as the catalysts involved are reviewed [210,211].

(18) Catalytic production of dimethylformamide from supercritical carbon dioxide. Methyl formate synthesis by hydrogenation of supercritical carbon dioxide in the presence of methanol. Selectivity for hydrogenation or hydroformylation of olefins by hydridopentacarbonyl manganese(I) in supercritical carbon dioxide. A review of the title research of P.G. Jessop, T. Ikariya, and R. Noyori (1994, 1995, and 1996) with commentary and one reference [212,213].

(19) The Fischer–Tropsch synthesis — molecular models for homogeneous catalysis? A review, with 31 references of research on molecular models and possible homogeneous variants of the heterogeneous Fischer–Tropsch reaction [214,215].

(20) Atropisomeric binaphthalene-core phosphacyclic derivatives in coordination chemistry and homogeneous catalysis. A review with 34 references [216,217].

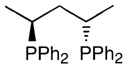
(21) Fluorous biphase systems, the new phase-separation and immobilization technique. A review with 21 references about application of fluorous biphase systems among others for hydroformylation [218].

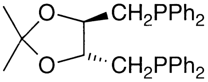
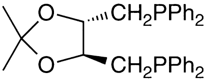
Acknowledgements

The author thanks the Hungarian Science Fund for support under Grant No. OTKA 16282 and the Hungarian Ministry of Culture and Education for support under Grant No. 0801/1997.

Appendix A

List of abbreviations

Ac	acetyl
acac	acetylacetonate
(+)-BDPP	

bpy	2,2′-bipyridine
^{c}Hx	cyclohexyl
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
(−)-DIOP	(2*R*,3*R*)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane 
(+)-DIOP	(2*S*,3*S*)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane 
DMF	*N*,*N*-dimethylformamide
DMSO	dimethylsulfoxide
dppb	$Ph_2PCH_2CH_2CH_2CH_2PPh_2$
dppe	$Ph_2PCH_2CH_2PPh_2$
dppm	$Ph_2PCH_2PPh_2$
dppp	$Ph_2PCH_2CH_2CH_2PPh_2$
ee	enantiomeric excess
hfacac	hexafluoroacetylacetonate
IR	infrared
py	pyridine
r.t.	room temperature
THF	tetrahydrofuran
TPPTS	trisodium salt of the trisulfonated triphenylphosphine
Ts	tosylate
wt%	weight per cent

The metals and their associated references are given in Appendix B.

Appendix B

Metal index: metal references

La	[89,90]
V	[168]
Cr	[136,137]
Mo	[136,137,168]
W	[136,137,171]
Mn	[86,87,212,213]
Fe	[77,78,152,219]
Ru	[76,88,172–175,180,193,194]

Co	[1–18,83,89–100,129,130,135,180]
Rh	[19–78,86,87,91–112,114–128,136–146,151,162–166,169,176–179,181,219]
Ir	[68,111–113,166]
Ni	[68]
Pd	[68,83,85,147–150,152–160,167,168,170]
Pt	[64,79–82,84,100,133,134,161]
Cu	[150,153,170]
Ag	[84,170]
Zn	[89,90]
Hg	[170]
Sn	[64,79–82,100,159,160]

References

[1] Y. Guo, A. Akgerman, Ind. Eng. Chem. Res. 36 (1997) 4581.
[2] Y. Guo, A. Akgerman, Chem. Abstr. 127 (1997) 264533.
[3] F. Piacenti, F. Calderazzo, M. Bianchi, L. Rosi, P. Frediani, Organometallics 16 (1997) 4235.
[4] Yu.T. Vigranenko, Zh. Prikl. Khim. (St.-Petersburg) 70 (1997) 618.
[5] Yu.T. Vigranenko, Chem. Abstr. 127 (1997) 96798.
[6] Yu.T. Vigranenko, V.M. Gavrilova, G.N. Gvozdovskii, V.A. Rybakov, G.V. Kuzmina, V.A. Pavlova, L.V. Bogdanova, Zh. Org. Khim. 32 (1996) 1832.
[7] Yu.T. Vigranenko, V.M. Gavrilova, G.N. Gvozdovskii, V.A. Rybakov, G.V. Kuzmina, V.A. Pavlova, L.V. Bogdanova, Chem. Abstr. 127 (1997) 83052.
[8] Yu.T. Vigranenko, V.A. Rybakov, V.V. Kashina, V.M. Gavrilova, G.N. Gvozdovskii, Kinet. Catal. (Transl. Kinet. Katal.) 37 (1996) 775.
[9] Yu.T. Vigranenko, V.A. Rybakov, V.V. Kashina, V.M. Gavrilova, G.N. Gvozdovskii, Chem. Abstr. 126 (1997) 103786.
[10] Yu.T. Vigranenko, M.G. Katsnel'son, Neftekhimiya 37 (1997) 224.
[11] Yu.T. Vigranenko, M.G. Katsnel'son, Chem. Abstr. 127 (1997) 358541.
[12] D. Li, K. Sun, X. Li, Y. Dong, Y. Dong, Y. Sun, Shiyou Huagong 26 (1997) 172.
[13] D. Li, K. Sun, X. Li, Y. Dong, Y. Dong, Y. Sun, Chem. Abstr. 126 (1997) 239856.
[14] D. Li, K. Sun, Y. Sun, Shiyou Huagong 26 (1997) 430.
[15] D. Li, K. Sun, Y. Sun, Chem. Abstr. 127 (1997) 222187.
[16] D. Li, Y. Kou, S. Liu, Y. Ma, Fenzi Cuihua 11 (1997) 180.
[17] D. Li, Y. Kou, S. Liu, Y. Ma, Chem. Abstr. 127 (1997) 196026.
[18] A. Cabrera, P. Sharma, J.L. Garcia, L. Velasco, F.J. Perez, J.L. Arias, N. Rosas, J. Mol. Catal. A: Chemical 118 (1997) 167.
[19] C. Botteghi, C. Lando, U. Matteoli, S. Paganelli, G. Menchi, J. Fluorine Chem. 83 (1997) 67.
[20] C. Botteghi, C. Lando, U. Matteoli, S. Paganelli, G. Menchi, Chem. Abstr. 127 (1997) 136087.
[21] F. Jiao, Q. Hu, Y. Chen, J. Niu, Y. Yin, Fenzi Cuihua 11 (1997) 145.
[22] F. Jiao, Q. Hu, Y. Chen, J. Niu, Y. Yin, Chem. Abstr. 126 (1997) 317112.
[23] J.A. Caldwell, Diss. Abstr. Int. B58 (1997) 833.
[24] J.A. Caldwell, Chem. Abstr. 127 (1997) 123621.
[25] J. Chen, A.N. Ajjou, R. Chanthateyanouth, H. Alper, Macromolecules 30 (1997) 2897.
[26] J. Chen, A.N. Ajjou, R. Chanthateyanouth, H. Alper, Chem. Abstr. 126 (1997) 293994.
[27] A.J. Solodar, E.D. Sall, L.E. Stout Jr., Chem. Ind. (Dekker) 68 (1996) 119.
[28] A.J. Solodar, E.D. Sall, L.E. Stout Jr., Chem. Abstr. 126 (1997) 9441.
[29] R. Della Pergola, L. Garlaschelli, S. Martinengo, A. Repossi, J. Mol. Catal. A: Chemical 115 (1997) 265.

[30] Y. Dong, C.A. Busacca, J. Org. Chem. 62 (1997) 6464.

[31] B.M. Bhanage, S.S. Divekar, R.M. Deshpande, R.V. Chaudhari, J. Mol. Catal. A: Chemical 115 (1997) 247.

[32] Z. Xia, C. Schobben, B. Fell, Fett/Lipid 98 (1996) 393.

[33] Z. Xia, C. Schobben, B. Fell, Chem. Abstr. 126 (1997) 145579.

[34] Z.G. Xia, B. Fell, J. Prakt. Chem./Chem.-Ztg. 339 (1997) 140.

[35] Z.G. Xia, B. Fell, Chem. Abstr. 126 (1997) 200881.

[36] C. Botteghi, M. Marchetti, S. Paganelli, B. Sechi, J. Mol. Catal. A: Chemical 118 (1997) 173.

[37] G.D. Cuny, S.L. Buchwald, Synlett (Spec. Issue) (1995) 519.

[38] G.D. Cuny, S.L. Buchwald, Chem. Abstr. 127 (1997) 190881.

[39] S.W. Kaldor, J.E. Fritz, J.A. Ward, Tetrahedron Lett. 38 (1997) 1509.

[40] M.M. Faul, B.E. Huff, S.E. Dunalp, S.A. Frank, J.E. Fritz, S.W. Kaldor, M.E. LeTourneau, M.A. Staszak, J.A. Jeffrey, J.A. Werner, L.L. Winneroski, Tetrahedron 53 (1997) 8085.

[41] M.M. Faul, B.E. Huff, S.E. Dunalp, S.A. Frank, J.E. Fritz, S.W. Kaldor, M.E. LeTourneau, M.A. Staszak, J.A. Jeffrey, J.A. Werner, L.L. Winneroski, Chem. Abstr. 127 (1997) 109139.

[42] G. Chelucci, M. Marchetti, B. Sechi, J. Mol. Catal. A: Chemical 122 (1997) 111.

[43] J. Andrade, J.J. Garcia, H. Torrens, F. del Rio, C. Claver, N. Ruiz, Inorg. Chim. Acta 255 (1997) 389.

[44] J.L.G. Fierro, M. Martínez-Ripoll, M.D. Merchón, A. Rodríguez, P. Terreros, H. Torrens, M.A. Vivar-Cerrato, J. Organomet. Chem. 544 (1997) 243.

[45] K.F. Muilwijk, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Am. Oil Chem. Soc. 74 (1997) 223.

[46] K.F. Muilwijk, P.C.J. Kamer, P.W.N.M. van Leeuwen, Chem. Abstr. 126 (1997) 279267.

[47] D.J. Bergman, E.M. Campi, W.R. Jackson, Q.J. McCubbin, A.F. Patti, Tetrahedron Lett. 38 (1997) 4315.

[48] S. Kainz, D. Koch, W. Baumann, W. Leitner, Angew. Chem., Int. Ed. Engl. 36 (1997) 1628.

[49] C.G. Arene, F. Nicolo, D. Drommi, G. Bruno, F. Faraone, J. Chem. Soc., Dalton Trans. (1996) 4357.

[50] A. Buhling, P.C.J. Kamer, P.W.N.M. van Leeuwen, J.W. Elgersma, Organometallics 16 (1997) 3027.

[51] A. Buhling, P.C.J. Kamer, P.W.N.M. van Leeuwen, J.W. Elgersma, J. Mol. Catal. A: Chemical 116 (1997) 297.

[52] G.J.H. Buisman, L.A. van der Veen, A. Klootwijk, W.G.J. de Lange, P.C.J. Kamer, P.W.N.M. van Leeuwen, D. Vogt, Organometallics 16 (1997) 2929.

[53] A. van Rooy, D. Burgers, P.C.J. Kamer, P.W.N.M. van Leeuwen, Recl. Trav. Chim. Pays-Bas 115 (1996) 492.

[54] A. van Rooy, D. Burgers, P.C.J. Kamer, P.W.N.M. van Leeuwen, Chem. Abstr. 126 (1997) 156956.

[55] A.M. Trzeciak, T. Glowiak, R. Grzybek, J.J. Ziolkowski, J. Chem. Soc., Dalton Trans. (1997) 1831.

[56] K. Nozaki, N. Sakai, T. Nanno, T. Higashijima, S. Mano, T. Horiuchi, H. Takaya, J. Am. Chem. Soc. 119 (1997) 4413.

[57] T. Horiuchi, E. Shirakawa, K. Nozaki, H. Takaya, Organometallics 16 (1997) 2981.

[58] T. Horiuchi, T. Ohta, E. Shirakawa, K. Nozaki, H. Takaya, J. Org. Chem. 62 (1997) 4285.

[59] K. Nozaki, W. Li, T. Horiuchi, H. Takaya, Tetrahedron Lett. 38 (1997) 4611.

[60] K. Nozaki, W. Li, T. Horiuchi, H. Takaya, Chem. Abstr. 127 (1997) 176306.

[61] T. Horiuchi, T. Ohta, E. Shirakawa, K. Nozaki, H. Takaya, Tetrahedron 53 (1997) 7795.

[62] T. Horiuchi, T. Ohta, E. Shirakawa, K. Nozaki, H. Takaya, Chem. Abstr. 127 (1997) 135361.

[63] B. Breit, Chem. Commun. (1997) 591.

[64] L. Kollár, E. Farkas, J. Bâtiu, J. Mol. Catal. A: Chemical 115 (1997) 283.

[65] A. Castellanos, S. Castillon, C. Claver, J. Organomet. Chem. 539 (1997) 1.

[66] R.W. Eckl, T. Priermeier, W.A. Herrmann, J. Organomet. Chem. 532 (1997) 243.

[67] M.T. Reetz, S.R. Waldvogel, R. Goddard, Tetrahedron Lett. 38 (1997) 5967.

[68] M.T. Reetz, G. Lohmer, R. Schwickardi, Angew. Chem., Int. Ed. Engl. 36 (1997) 1526.

[69] C.P. Casey, E.L. Paulsen, E.W. Beuttenmueller, B.R. Proft, C.M. Petrovich, B.A. Matter, D.R. Powell, J. Am. Chem. Soc. 119 (1997) 11817.

[70] B. Breit, R. Winde, K. Harms, J. Chem. Soc., Perkin Trans. 1 (1997) 2681.

[71] J.L. Leighton, D.N. O'Neil, J. Am. Chem. Soc. 119 (1997) 11118.

[72] E.A. Karakhanov, Yu.S. Kardasheva, E.B. Neimerovets, E.A. Runova, Vestn. Mosk. Univ., Ser. 2: Khim. 37 (1996) 533.
[73] E.A. Karakhanov, Yu.S. Kardasheva, E.B. Neimerovets, E.A. Runova, Chem. Abstr. 127 (1997) 331175.
[74] T. Müller, H. Bahrmann, J. Mol. Catal. A: Chemical 116 (1997) 39.
[75] T. Matsubara, N. Koga, Y. Ding, D.G. Musaev, K. Morokuma, Organometallics 16 (1997) 1065.
[76] P. Frediani, M. Bianchi, A. Salvini, L.C. Carluccio, L. Rosi, J. Organomet. Chem. 547 (1997) 35.
[77] H.C. Bottcher, K. Merzweiler, C. Bruhn, Z. Naturforsch. b: Chem. Sci. 52 (1997) 810.
[78] H.C. Bottcher, K. Merzweiler, C. Bruhn, Chem. Abstr. 127 (1997) 199226.
[79] S. Cserépi-Szücs, J. Bakos, Chem. Commun. (1997) 635.
[80] J. Fopрniés-Cámer, A. Aaliti, N. Ruiz, A.M. Masdeu-Bultó, C. Claver, C.J. Cardin, J. Organomet. Chem. 530 (1997) 199.
[81] I. Tóth, C.J. Elsevier, J.G. deVries, J. Bakos, W.J.J. Smeets, A.L. Spek, J. Organomet. Chem. 540 (1997) 15.
[82] A. de O. Dias, R. Augusti, E.N. dos Santos, E.V. Gusevskaya, Tetrahedron Lett. 38 (1997) 41.
[83] Y. Ishii, K. Miyashita, K. Kamita, M. Hidai, J. Am. Chem. Soc. 119 (1997) 6448.
[84] T. Kégl, L. Kollár, J. Mol. Catal. A: Chemical 122 (1997) 95.
[85] W.-Y. Yu, H. Alper, J. Org. Chem. 62 (1997) 5684.
[86] S.S.C. Chuang, M.A. Brundage, M.W. Balakos, Appl. Catal. A15 (1997) 333.
[87] S.S.C. Chuang, M.A. Brundage, M.W. Balakos, Chem. Abstr. 126 (1997) 199191.
[88] F.-S. Xiao, M. Ichikawa, J. Mol. Catal. A: Chemical 113 (1996) 427.
[89] J. Llorca, A. Barbier, G.A. Martin, J. Sales, R. de la Piscina, N. Homs, Catal. Lett. 42 (1996) 87.
[90] J. Llorca, A. Barbier, G.A. Martin, J. Sales, R. de la Piscina, N. Homs, Chem. Abstr. 126 (1997) 30994.
[91] L. Huang, A. Liu, Y. Xu, J. Mol. Catal. A: Chemical 124 (1997) 57.
[92] L. Huang, J. Mol. Catal. A: Chemical 125 (1997) 47.
[93] L. Huang, Y.-D. Xu, J. Nat. Gas Chem. 6 (1997) 188.
[94] L. Huang, Y.-D. Xu, Chem. Abstr. 127 (1997) 249662.
[95] L. Huang, Y.-D. Xu, J. Nat. Gas Chem. 6 (1997) 198.
[96] L. Huang, Y.-D. Xu, Chem. Abstr. 127 (1997) 242385.
[97] L. Huang, Y. Xu, React. Kinet. Catal. Lett. 61 (1997) 397.
[98] Z. Xia, U. Kloeckner, B. Fell, Fett/Lipid 98 (1996) 313.
[99] Z. Xia, U. Kloeckner, B. Fell, Chem. Abstr. 126 (1997) 9456.
[100] I. Tóth, I. Guo, B.E. Hanson, J. Mol. Catal. A: Chemical 116 (1997) 217.
[101] J.R. Anderson, E.M. Campi, W.R. Jackson, Z.P. Yang, J. Mol. Catal. A: Chemical 116 (1997) 109.
[102] J.R. Anderson, W.R. Jackson, Z.P. Yang, E.M. Campi, Catal. Lett. 45 (1997) 197.
[103] J.R. Anderson, W.R. Jackson, Z.P. Yang, E.M. Campi, Chem. Abstr. 127 (1997) 109233.
[104] D. Cauzzi, M. Costa, L. Gonzalvi, M.A. Pellinghelli, G. Predieri, A. Tripicchio, R. Zanoni, J. Organomet. Chem. 541 (1997) 377.
[105] G.V. Terekhova, N.V. Kolesnichenko, E.D. Alieva, N.A. Markova, N.I. Trukhmanova, E.V. Slivinskii, N.A. Plate, Izv. Akad. Nauk, Ser. Khim. (1996) 1673.
[106] G.V. Terekhova, N.V. Kolesnichenko, E.D. Alieva, N.A. Markova, N.I. Trukhmanova, E.V. Slivinskii, N.A. Plate, Chem. Abstr. 126 (1997) 30985.
[107] N.V. Kolesnichenko, G.V. Terekhova, A.T. Teleshev, E.I. Alekseeva, E.V. Slivinskii, Russ. Chem. Bull. (Transl. Izv. Akad. Nauk, Ser. Khim.) 46 (1997) 1107.
[108] N.V. Kolesnichenko, G.V. Terekhova, A.T. Teleshev, E.I. Alekseeva, E.V. Slivinskii, Chem. Abstr. 127 (1997) 333059.
[109] N. Yoneda, Y. Nakagawa, T. Mimami, Catal. Today 36 (1997) 357.
[110] N. Yoneda, Y. Nakagawa, T. Mimami, Chem. Abstr. 127 (1997) 19897.
[111] S. Bischoff, A. Weigt, M. Kant, U. Schuelke, B. Luecke, Catal. Today 36 (1997) 273.
[112] S. Bischoff, A. Weigt, M. Kant, U. Schuelke, B. Luecke, Chem. Abstr. 127 (1997) 19899.
[113] T. Shido, T. Okazaki, M. Ichikawa, J. Mol. Catal. A: Chemical 120 (1997) 33.
[114] J. Chen, H. Alper, J. Am. Chem. Soc. 119 (1997) 893.
[115] H. Ding, J. Kang, B.E. Hanson, C.W. Kohlpaintner, J. Mol. Catal. A: Chemical 124 (1997) 21.

[116] R.M. Deshpande, P. Purwanto, H. Delmas, R.V. Chaudhari, J. Mol. Catal. A: Chemical 126 (1997) 133.
[117] N.V. Kolesnichenko, M.V. Shirikova, T.K. Murzabekova, N.A. Markova, E.V. Slivinskii, Izv. Akad. Nauk, Ser. Khim. (1996) 1968.
[118] N.V. Kolesnichenko, M.V. Shirikova, T.K. Murzabekova, N.A. Markova, E.V. Slivinskii, Chem. Abstr. 126 (1997) 89057.
[119] H. Bahrmann, M. Haubs, T. Müller, N. Schöpper, B. Cornils, J. Organomet. Chem. 545–546 (1997) 139.
[120] H. Bahrmann, C.D. Frohning, P. Heymanns, H. Kalbfell, P. Lappe, D. Peters, E. Wiebus, J. Mol. Catal. A: Chemical 116 (1997) 35.
[121] Z. Jin, X. Zeng, B. Fell, J. Mol. Catal. A: Chemical 116 (1997) 55.
[122] J. Li, H. Zhou, S. Huang, P. Lin, L. Lin, Cuihua Xuebao 18 (1997) 318.
[123] J. Li, H. Zhou, S. Huang, P. Lin, L. Lin, Chem. Abstr. 127 (1997) 249681.
[124] E.A. Karakhanov, Yu.S. Kardasheva, E.B. Neimerovets, E.A. Runova, Neftekhimiya 36 (1996) 321.
[125] E.A. Karakhanov, Yu.S. Kardasheva, E.B. Neimerovets, E.A. Runova, Chem. Abstr. 126 (1997) 117723.
[126] M.V. Sharikova, N.A. Markova, V.V. Kolesnichenko, A.T. Teleshev, E.V. Slivinskii, L.A. Vytnova, Neftekhimiya 36 (1996) 422.
[127] M.V. Sharikova, N.A. Markova, V.V. Kolesnichenko, A.T. Teleshev, E.V. Slivinskii, L.A. Vytnova, Chem. Abstr. 126 (1997) 185782.
[128] M.T. Reetz, S.R. Waldvogel, Angew. Chem., Int. Ed. Engl. 36 (1997) 865.
[129] U. Ritter, GIT Fachz. Lab. 40 (1996) 969.
[130] U. Ritter, Chem. Abstr. 126 (1997) 95306.
[131] H. Oliver, Y. Chauvin, Chem. Ind. (Dekker) 68 (1996) 249.
[132] H. Oliver, Y. Chauvin, Chem. Abstr. 126 (1997) 46733.
[133] K. Otsuka, T. Ando, I. Yamanaka, J. Catal. 165 (1997) 221.
[134] K. Otsuka, T. Ando, I. Yamanaka, Chem. Abstr. 126 (1997) 217723.
[135] L. Rosi, A. Salvini, M. Bianchi, P. Frediani, F. Piacenti, J. Organomet. Chem. 535 (1997) 143.
[136] K.J. Coutinho, R.S. Dickson, G.D. Fallon, W.R. Jackson, T. De Simone, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1997) 3193.
[137] K.J. Coutinho, R.S. Dickson, G.D. Fallon, W.R. Jackson, T. De Simone, B.W. Skelton, A.H. White, Chem. Abstr. 127 (1997) 319053.
[138] D. Liao, Y. Lin, Z. Huang, Y. Peng, Xiamen Daxue Xuebao, Ziran Kexueban 35 (1996) 445.
[139] D. Liao, Y. Lin, Z. Huang, Y. Peng, Chem. Abstr. 126 (1997) 149091.
[140] P. Schmid, W.A. Herrmann, G. Frenking, Organometallics 16 (1997) 701.
[141] A. van Rooy, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Organomet. Chem. 535 (1997) 201.
[142] J. Rankin, A.D. Poole, A.C. Bényei, D.J. Cole-Hamilton, Chem. Commun. (1997) 1835.
[143] J.L. Leighton, E. Chapman, J. Am. Chem. Soc. 119 (1997) 12416.
[144] I. Matsuda, Y. Fukuta, T. Tsuchihashi, H. Nagashima, K. Itoh, Organometallics 16 (1997) 4327.
[145] M. Tzamarioudaki, Diss. Abstr. Int. B57 (1997) 6943.
[146] M. Tzamarioudaki, Chem. Abstr. 126 (1997) 293078.
[147] W. Keim, J. Herwig, G. Pelzer, J. Org. Chem. 62 (1997) 422.
[148] E. Monflier, S. Tilloy, F. Bertoux, Y. Castanet, A. Mortreux, New J. Chem. 21 (1997) 857.
[149] E. Monflier, S. Tilloy, F. Bertoux, Y. Castanet, A. Mortreux, Chem. Abstr. 127 (1997) 292878.
[150] J.-Y. Yoon, E.J. Jang, K.H. Lee, J.S. Lee, J. Mol. Catal. A: Chemical 118 (1997) 181.
[151] T. Mizuno, H. Alper, J. Mol. Catal. A: Chemical 123 (1997) 21.
[152] S. Oi, M. Nomura, T. Aiko, Y. Inoue, J. Mol. Catal. A: Chemical 115 (1997) 289.
[153] H. Zhou, J. Hou, J. Cheng, S. Lu, H. Fu, H. Wang, J. Organomet. Chem. 543 (1997) 227.
[154] A.V. Zeigarnik, R.E. Valdes-Perez, O.N. Temkin, L.G. Bruk, S.I. Shalgunov, Organometallics 16 (1997) 3114.
[155] S. Tilloy, E. Monflier, F. Bertoux, Y. Castanet, A. Mortreux, New J. Chem. 21 (1997) 529.
[156] S. Tilloy, E. Monflier, F. Bertoux, Y. Castanet, A. Mortreux, Chem. Abstr. 127 (1997) 135459.
[157] G. Papadogianakis, G. Verspui, L. Maat, R.A. Sheldon, Catal. Lett. 47 (1997) 43.
[158] G. Papadogianakis, G. Verspui, L. Maat, R.A. Sheldon, Chem. Abstr. 127 (1997) 277806.

[159] Yu.G. Noskov, E.S. Petrov, Kinet. Catal. (Transl. Kinet. Katal.) 38 (1997) 520.
[160] Yu.G. Noskov, E.S. Petrov, Chem. Abstr. 127 (1997) 277872.
[161] A. Ogawa, J. Kawakami, M. Mihara, T. Ikeda, N. Sonoda, T. Hirao, J. Am. Chem. Soc. 119 (1997) 12380.
[162] T. Sakakura, K. Ishiguro, M. Okano, T. Sako, Chem. Lett. (1997) 1089.
[163] M. Mediavilla, A.J. Pardey, P. Baricelli, C. Longo-Pardey, S.A. Moya, Rhodium Express 15 (1996) 9.
[164] M. Mediavilla, A.J. Pardey, P. Baricelli, C. Longo-Pardey, S.A. Moya, Chem. Abstr. 126 (1997) 95326.
[165] T. Mizugaki, K. Ebitani, K. Kaneda, Tetrahedron Lett. 38 (1997) 3005.
[166] A.M. Kelly, G.P. Rosini, A.S. Goldman, J. Am. Chem. Soc. 119 (1997) 6115.
[167] G. Cavinato, M. Pasqualetto, L. Ronchin, L. Toniolo, J. Mol. Catal. A: Chemical 125 (1997) 15.
[168] F. Ragaini, M. Macchi, S. Cenini, J. Mol. Catal. A: Chemical 127 (1997) 33.
[169] T. Mizuno, H. Alper, J. Mol. Catal. A: Chemical 121 (1997) 119.
[170] R. Santi, A.M. Romano, F. Panella, C. Santini, J. Mol. Catal. A: Chemical 127 (1997) 95.
[171] N. Endo, Y. Miho, K. Ogura, J. Mol. Catal. A: Chemical 127 (1997) 49.
[172] K. Kasuga, M. Terauchi, M. Hara, K. Nishie, T. Sugimori, M. Handa, Bull. Chem. Soc. Jpn. 70 (1997) 2107.
[173] K.-I. Tominaga, Y. Sasaki, T. Watanabe, M. Saito, Energy (Oxford) 22 (1997) 169.
[174] K.-I. Tominaga, Y. Sasaki, T. Watanabe, M. Saito, Chem. Abstr. 126 (1997) 136239.
[175] O. Kröcher, R.A. Köppel, A. Baiker, Chem. Commun. (1997) 453.
[176] E. Lindner, B. Keppeler, P. Wegner, Inorg. Chim. Acta 258 (1997) 97.
[177] K. Angermund, W. Baumann, E. Dinjus, R. Fornika, H. Görls, M. Kessler, C. Krüger, W. Leitner, F. Lutz, Chem. Eur. J. 3 (1997) 755.
[178] K. Angermund, W. Baumann, E. Dinjus, R. Fornika, H. Görls, M. Kessler, C. Krüger, W. Leitner, F. Lutz, Chem. Abstr. 127 (1997) 130049.
[179] F. Hutschka, A. Dedieu, M. Eichberger, R. Fornika, W. Leitner, J. Am. Chem. Soc. 119 (1997) 4432.
[180] M. Reinikainen, J. Kiviaho, M. Kroeger, M. Niemelae, S. Jaeaeskelaeinen, J. Mol. Catal. A: Chemical 118 (1997) 137.
[181] N. Chatani, M. Shinohara, S. Ikeda, S. Murai, J. Am. Chem. Soc. 119 (1997) 4303.
[182] C.D. Frohning, C.W. Kohlpaintner, Appl. Homogeneous Catal. Organomet. Compd. 1 (1996) 29.
[183] C.D. Frohning, C.W. Kohlpaintner, Chem. Abstr. 127 (1997) 190439.
[184] W.A. Herrmann, B. Cornils, Angew. Chem., Int. Ed. Engl. 36 (1997) 1048.
[185] I. Wender, Fuel Process. Technol. 48 (1996) 189.
[186] I. Wender, Chem. Abstr. 126 (1997) 48930.
[187] V.I. Yakerson, E.Z. Golosman, Actual Probl. Proizvod. Katal. Prom. Katal., Tr. Semin. 1 (2) (1994) 31.
[188] V.I. Yakerson, E.Z. Golosman, Chem. Abstr. 126 (1997) 119302.
[189] C. Botteghi, M. Marchetti, G. Del Ponte, Quim. Nova 20 (1997) 30.
[190] C. Botteghi, M. Marchetti, G. Del Ponte, Chem. Abstr. 126 (1997) 330221.
[191] S. Törös, Kém. Közl. 83 (1997) 171.
[192] S. Törös, Chem. Abstr. 126 (1997) 225443.
[193] T. Mitsudo, Yuki Gosei Kagaku Kenkyusho Koenshu 11 (1997) 60.
[194] T. Mitsudo, Chem. Abstr. 126 (1997) 305289.
[195] W. Shen, C. Wang, J. Zhou, B. Zhang, Tianranqi Huagong 21 (1996) 32.
[196] W. Shen, C. Wang, J. Zhou, B. Zhang, Chem. Abstr. 126 (1997) 318639.
[197] H.-L. Wan, Y.-Z. Yuan, J.-X. Gao, H.-B. Zhang, K. Tsai, Gaodeng Xuexiao Huaxue Xuebao 18 (1997) 1185.
[198] H.-L. Wan, Y.-Z. Yuan, J.-X. Gao, H.-B. Zhang, K. Tsai, Chem. Abstr. 127 (1997) 71274.
[199] F. Joó, Á. Kathó, J. Mol. Catal. A: Chemical 116 (1997) 3.
[200] D.E. Paez, Vision Technol. 4 (1997) 147.
[201] D.E. Paez, Chem. Abstr. 127 (1997) 83522.
[202] B. Cornils, W.A. Herrmann, R.W. Eckl, J. Mol. Catal. A: Chemical 119 (1997) 27.
[203] Y. Chauvin, Actual Chim. (1996) 44.

[204] Y. Chauvin, Chem. Abstr. 126 (1997) 95293.
[205] Z. Fang, Shiyou Huagong 26 (1997) 479.
[206] Z. Fang, Chem. Abstr. 127 (1997) 177927.
[207] H. Bahrmann, H. Bach, C.D. Frohning, H.J. Kleiner, P. Lappe, D. Peters, D. Regnat, W.A. Herrmann, J. Mol. Catal. A: Chemical 116 (1997) 49.
[208] W.A. Herrmann, Appl. Homogeneous Catal. Organomet. Compd. 2 (1996) 957.
[209] W.A. Herrmann, Chem. Abstr. 127 (1997) 167332.
[210] M. Beller, A.M. Tafesh, Appl. Homogeneous Catal. Organomet. Compd. 1 (1996) 187.
[211] M. Beller, A.M. Tafesh, Chem. Abstr. 127 (1997) 205134.
[212] C. Bianchini, L. Glendenning, Chemtracts: Org. Chem. 9 (1996) 318.
[213] C. Bianchini, L. Glendenning, Chem. Abstr. 126 (1997) 131047.
[214] W.A. Herrmann, Appl. Homogeneous Catal. Organomet. Compd. 2 (1996) 747.
[215] W.A. Herrmann, Chem. Abstr. 127 (1997) 150746.
[216] S. Gladiali, D. Fabbri, Chem. Ber./Recl. 130 (1997) 543.
[217] S. Gladiali, D. Fabbri, Chem. Abstr. 126 (1997) 343585.
[218] B. Cornils, Angew. Chem., Int. Ed. Engl. 36 (1997) 2057.
[219] R. Della Pergola, A. Cinquantini, E. Diana, L. Garlaschelli, F. Laschi, P. Luzzini, M. Manassero, A. Repassi, M. Sansoni, P.L. Stanghellini, P. Zanello, Inorg. Chem. 36 (1997) 3761.