Coordination Chemistry Reviews
188 (1999) 263–296

COORDINATION
CHEMISTRY
REVIEWS

www.elsevier.com/locate/ccr

Application of transition metals in hydroformylation annual survey covering the year 1998

Ferenc Ungváry

Department of Organic Chemistry,
University of Veszprém and Research Group for Petrochemistry of the Hungarian Academy of Sciences, H-8200 Veszprém, Egyetem u. 10, Hungary

Accepted 11 January 1999

Contents

PII: S0010-8545(99)00037-5

Abstract

Hydroformylation in homogeneous and heterogeneous systems, and hydroformylation related reactions of carbon monoxide are reviewed.

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

---

1. Hydroformylation

1.1. Homogeneous systems

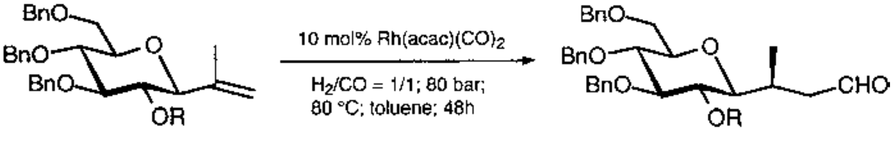
1.1.1. Cobalt catalysts

The catalytic activity of $Co_2(CO)_6L_2$ complexes (L = carbon monoxide, phosphines) was tested in the oligomerization of aldehydes under the conditions adopted for hydroformylation of olefins. Transformation of typical aldehydes such as n-butanal was investigated in the presence and in the absence of the cobalt complexes $Co_2(CO)_6L_2$ in order to distinguish the relevance of the cobalt-catalyzed and/or of the pure thermal reaction. The positive role of cobalt carbonyl complexes in the aldehyde oligomerization was rationalized by a mechanism, in which acylcobalt intermediates are involved [1]. See also Ref. [42].

1.1.2. Rhodium catalysts

Typical sources of error and the magnitude of these errors in evaluation of turnover frequencies from analysis of in situ infrared spectroscopic measurements of the homogeneous rhodium-catalyzed hydroformylation of alkenes has been discussed in detail [2].

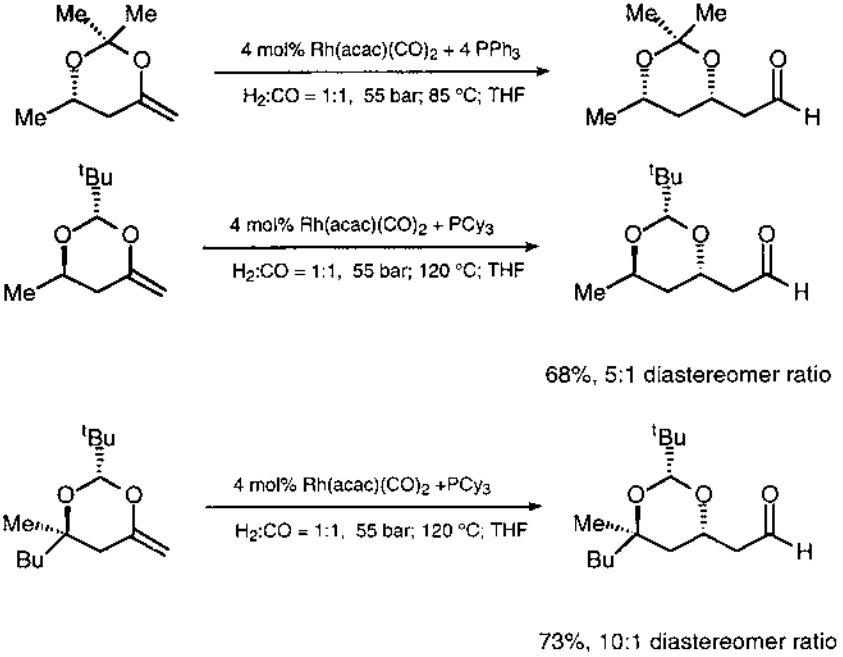
Hydroformylation of 1,1-disubstituted C-glycosylated olefins **1** gave β-substituted aldehydes **2** in good to excellent yields with ≤ 99%, diastereoselectivity [3].



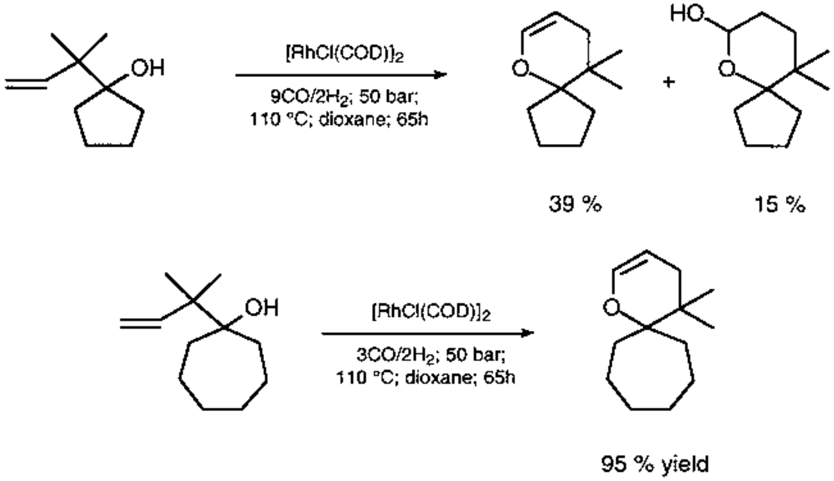
1 (R = H, Piv, Bz, Ac, TBS) **2** 81-99% yield

Hydroformylation of styrene was studied in the presence of triphenylphosphine and chiral diphosphine ligands using 0.25 mol% of the complex $[Rh_2(\mu\text{-pz})(\mu\text{-S}^t\text{Bu})(COD)_2]$ (pz = pyrazolate) as the catalyst precursor. When triphenylphosphine is used as the phosphorus ligand complete conversion to aldehydes and regioselectivities as high as 90% in 2-phenylpropanal are obtained at 80°C and 5–30 bar $CO:H_2 = 1:1$ pressure. The use of BDPP (BDPP = bis(diphenylphosphino)pentane) as a chiral diphosphine in a P/Rh ratio of 2 provides 95% regioselectivity and enentiomeric excess as high as 50% [4].

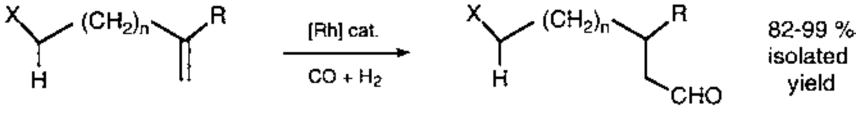
Conformational effects on the regioselectivity of olefin insertion in the rhodium-catalyzed hydroformylation of 4-methylene-1,3-dioxanes have been reported [5], e.g.:



A convenient preparation of substituted spiropyrans by using a one-pot rhodium-catalyzed hydroformylation/hemiacetal/elimination sequence starting from homoallylic alcohols, has been described [6], e.g.:



The rhodium-catalyzed hydroformylation of ω-functionalized 1,1-disubstituted alkenes **3** at 40 or 60°C and 80 bar CO:H_2 = 1:1 using 5 mol% of Rh(acac)$(CO)_2$ as the catalyst precursor in toluene was found to give the corresponding linear aldehydes **4** in good yields [7].

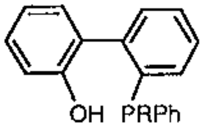


3 **4**

where R = Me; $n = 11$; X = OTs, OH, Br, ^{t}BuMe$_2$Si, EtOCH$_2$CH$_2$ and R = Et, ^{i}Pr, ^{t}Bu; X = OH.

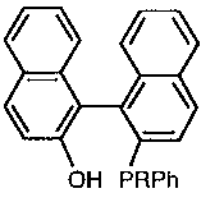
The rhodium-catalyzed hydroformylation of 1-hexene in THF in the presence of the triphosphine PhP$(CH_2CH_2PPh_2)_2$ was studied both in situ and in high-pressure autoclaves. For studying the in situ reactions under conditions of relatively high syngas pressure (30–90 bar CO/H_2) and temperature (60–100°C) sapphire NMR tubes with titanium valves have proved to be useful. It was found that irrespective of the syngas composition and of the total pressure, the dicarbonyl complex $[PhP(CH_2CH_2)PPh_2)_2Rh(CO)_2]^+$ is the only phosphorus-containing species detectable on the NMR time-scale during the course of the isomerization and hydroformylation of the alkene. Some peculiar features of the catalytic system were summarized as follows. (a) High partial pressures (120 bar) of carbon monoxide neither inhibit the hydroformylation nor affect the normal/iso selectivity; (b) alkene hydroformylation does not occur at very high partial pressures of H_2 or in the absence of added carbon monoxide; (c) the rate of isomerization of the 1-alkene is only slightly faster than that of hydroformylation; (d) terminal and internal alkenes (2- and 3-hexenes) are hydroformylated with comparable rates [8].

Comparative screening tests of 2′-phosphanyl-1,1′-biphenyl-2-ols (**5**) and 2′-phosphanyl-1,1′-binaphthyl-2-ols (**6**) in homogeneous rhodium-catalyzed hydroformylation reactions of vinyl acetate at 80°C and 50 bar have shown that these ligands exhibit a higher activity than other P–O ligands [9].



(R = Ph, Me, ^{i}Pr, ^{t}Bu)

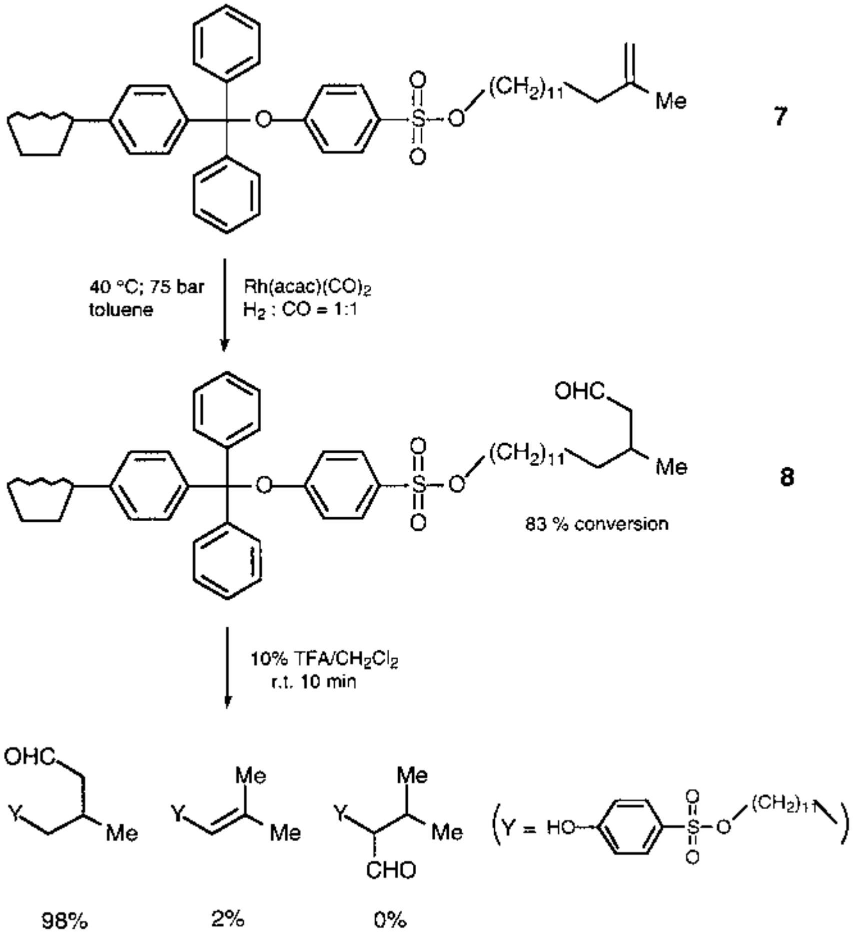
5



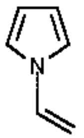
(R = Ph, ^{i}Pr,)

6

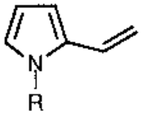
Rhodium(I)-catalyzed hydroformylation of a polymer-supported 1,1-disubstituted alkene **7**, consisting of a polystyrene-grafted crown connected to the olefin by a trityl linker and a traceless linker, was carried out under 75 bar of $CO:H_2 = 1:1$, providing the corresponding aldehyde **8** on the solid support. Optimization of the reaction conditions is described [10].



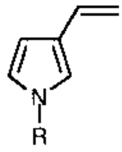
The influence of the temperature on the regioselectivity in the hydroformylation of the vinylpyrroles **9**–**11** has been investigated in the range of 20–100°C at 120 bar $CO/H_2 = 1:1$ using $Rh_4(CO)_{12}$ as the catalyst precursor. The formation of the branched aldehyde prevailed in all cases at all the temperatures applied. With increasing temperature, however, an increase of the proportion of the linear aldehyde was observed. ^{2}H-NMR investigation of the reaction product from deuteroformylation of 3-vinylpyrrole has shown that the observed change in regioselectivity with increasing temperature is probably associated with a β-hydride elimination process occurring for the branched alkyl-rhodium intermediate but not for the linear ones [11].



9



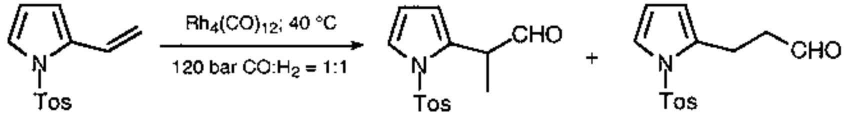
10



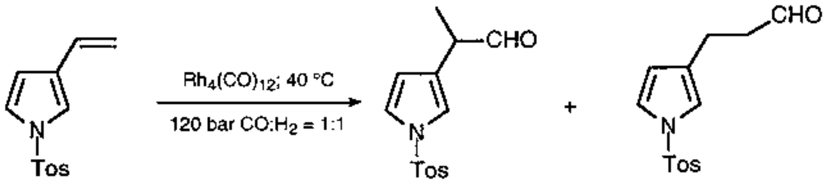
11

(R = H, Tos)

Hydroformylation of 2-vinyl- and 3-vinyl-1-tosylpyrroles gives the corresponding 2-(1-tosylpyrrolyl)propanals in 70% yield [12].



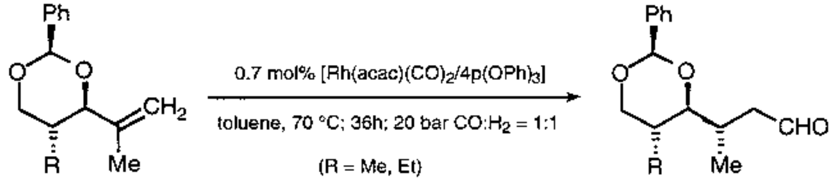
94 : 6



96 : 4

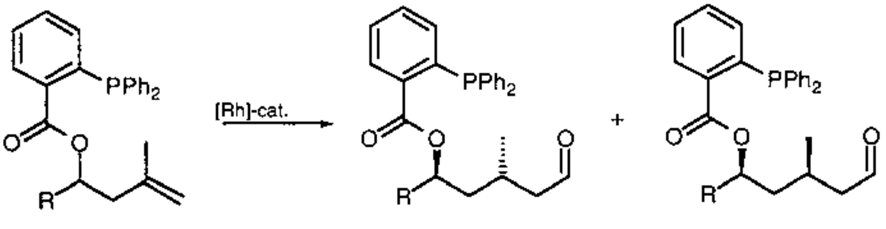
In the $Rh_4(CO)_{12}$-catalyzed hydroformylation of the vinylpyridine isomers, a very different chemoselectivity between 3- and 4-vinylpyridine was observed. At 60 or 100°C and 100 bar CO/H_2 pressure 3-vinylpyridine gave predominantly the branched aldehyde with $>99\%$ selectivity, whereas 4-vinylpyridine under the same conditions gave with $>98\%$ selectivity the hydrogenation product 4-ethylpyridine [13].

The rhodium-catalyzed hydroformylation of the benzylidene acetals **12** gave the aldehydes **13** in 80% yields and with complete diastereoselectivity ($\geq 99\%$) [14].



12 **13**

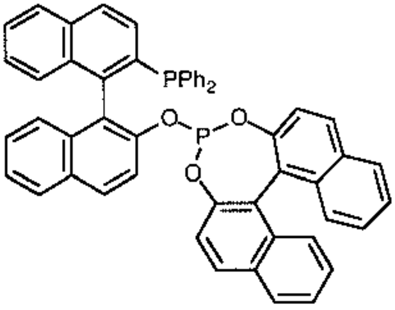
The *ortho*-diphenylphosphinylbenzoate group (*o*-DPPB) was found to be an effective catalyst-directing group in the rhodium-catalyzed stereoselective hydroformylation of acyclic homomethallylic alcohols. Thus, hydroformylation of the *o*-DPPB-ester in the presence of 0.7 mol% [Rh(acac)(CO)$_2$] and 2.8 mol% P(OPh)$_3$ at 20 bar $H_2/CO = 1:1$ in toluene at 30–50°C gave the corresponding aldehydes **14** in good to excellent yields (73–93%) and with anti-diastereoselectivities of up to 91% [15].



14 **anti-15** **syn-15**

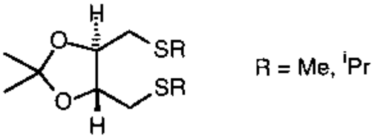
(R = Me, ^{c}Hx, ^{n}Hx, Ph, 2-MeO-C_6H_4, *E*-1-Methylbut-1-enyl)

A semiquantitative theoretical model was used to elucidate the origin of stereodifferentiation in rhodium-BINAPHOS-catalyzed hydroformylation. (BINAPHOS = **16**). It was demonstrated that the outstanding properties of BINAPHOS are due to the synergistic combination of the pronounced coordination preferences for steric and electronic reasons, to the adequate number of chirality centers, and to the correct configuration of the binaphthyl fragments [16].



16

A chiral phosphinite ligand derived from β-cyclodextrin was used as the ligand in rhodium-catalyzed asymmetric hydroformylation of vinyl acetate. Effects of reaction temperature, pressure, solvent, and molar ratio of P to Rh were investigated. When the asymmetric hydroformylation of vinyl acetate was carried out at 80°C, 70 bar $CO:H_2 = 1:1$, P/Rh = 3.37 for 24 h, the branched aldehyde was formed selectively with 27.4% ee [17].Cationic rhodium complexes with dithioethers **17** as chiral ligands were tested as catalyst precursors in styrene hydroformylation at 30 bar and 65°C. Although conversions of up to 99% with a regioselectivity in 2-phenylpropanal as high as 74% were achieved, the enantioselectivities were low (3–6%) [18].



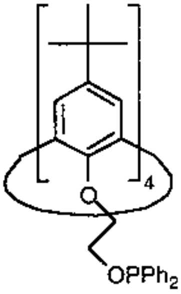
17

Asymmetric hydroformylation of styrene was performed using rhodium complexes of the atropisomeric racemic sulfur compound 4,4′-biphenanthrene-3,3′-dithiol as the catalyst precursors. The observed extent of aldehyde conversion was between 53 and 100%, with selectivities towards the branched aldehyde between 53 and 96%. The enantioselectivities, however, were low and did not exceed 20% [19]. Hydroformylation of optically pure monoterpenes using dinuclear thiolato-bridged rhodium complexes $[Rh_2(\mu\text{-}S\text{–}{}^tBu)_2(CO)_2L_2]$ was studied. ($L = P(OPh)_3$, PPh_3, $L_2 = Ph_2PCH_2CH_2CH_2CH_2CH_2CH_2PPh_2$, (−)-DIOP, (−) BDPP). The exocyclic ethylenic double bond of (R)-limonene, (S)-carvone, (S)-perillyl alcohol, or (1R,4R)-isolimonene gave at 5–13 bar pressure a 22% diastereomeric excess under the best conditions. Cyclization following the hydroformylation of (1R,2S,5R)-isopulegol led to a 64% diasteromeric excess. This reaction does not require the presence of chiral phosphorus ligands. The asymmetric induction is directed by the substrate configuration. (−)-β-Pinene and (−)-camphene were selectively carbonylated at 13–20 bar pressure and diastereomeric excesses ranging from 26 to 85% were obtained with classical phosphite or diphosphine ligands. (−)-α-Pinene and (−) myrtenol were transformed at 100 bar with moderate yields and selectivities but high diastereomeric excesses of up to 100% was observed [20].

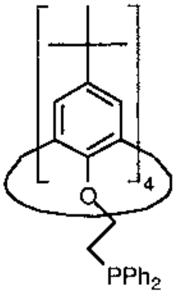
A catalyst prepared in situ from $Rh_2(OAc)_4$ and triethylphosphine was used for the hydroformylation of 1-hexene in supercritical carbon dioxide. At 100°C, $P(CO) = P(H_2) = 20$ bar and $[Rh] = 6.5 \times 10^{-3}$ M, complete conversion to C_7 aldehydes, with a trace of C_7 alcohols (total straight to branched ratio = 2.4) was obtained in 2 h [21]. Rhodium(II) complexes with the monoanion of dimethylglyoxime, $[Rh(Hdmg)_2(PPh_3)]_2$ and $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$ were used as catalyst precursors in the hydroformylation of 1-hexene at 10 bar CO/H_2 and 80°C. Hydroformylation in the presence of $[Rh(Hdmg)_2(PPh_3)]_2$ produces 94% of aldehydes (normal/iso = 2.2) and 6% 2-hexene, whereas using $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$ gives ca. 40% aldehyde (normal/iso = 2.1) and 60% of 2-hexene [22]. Dicarbonylsalicylaldoximatorhodium dicarbonyl combined with phosphorous ligands was found to exhibit high activity for hydroformylation of olefins under mild conditions. In the case of styrene, almost pure branched aldehyde 2-phenylpropanal was obtained. Hydroformylation of 1-hexene gave mainly n-heptanal. The effect of mono- and diphosphines and of the CO/H_2 ratio on the activity and regioselectivity was investigated [23].

Polyoxyethylenes containing a PPh, PPh_2, or $P(OPh)_2$ end group were used as ligands in rhodium-catalyzed hydroformylation of 1-dodecene at 50°C and 1–15 bar pressure. The effects of temperature, pressure, and P/Rh ratio in the catalyst were studied [24].

The catalytic systems formed in situ from $PtCl_2(PhCN)_2$, $[Rh(NBD)Cl]_2$ and $PdCl_2(PhCN)_2$ and the calixarene ligands **18** and **19** were tested as catalysts in hydroformylation and hydrocarbalkoxylation, respectively. High chemoselectivity (96.8–99.9%) towards aldehydes was obtained in hydroformylation of styrene in the presence of rhodium-containing catalysts with both calixarene-based phosphine and phosphinite ligands. The regioselectivity towards branched aldehyde was found to be strongly dependent on the temperature in case of phosphinite ligand **19**. Thus, up to 92.6% 2-phenyl-propanal was obtained at 55°C, which drops to 57% at 135°C. The platinum-containing systems show much lower catalytic activity, but the regioselectivities are higher (40–50%) than those obtained with $PtCl_2$(diphosphine)–$SnCl_2$ systems. Hydroalkoxycarbonylation of styrene in the presence of the platinum-**18** system in methanol or *tert*-butanol at 130°C and 140 bar CO gave 47–62% regioselectivity towards the branched ester [25].



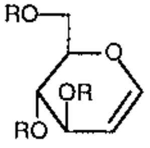
18



19

Bisphosphinite–rhodium(I) complexes were used as catalysts in the hydroformylation of styrene and of 2-vinylnaphthalene [26]. Hydroformylation of styrene and *p*-methylstyrene was investigated using $Rh(acac)(CO)_2$ as catalyst precursor in the presence of various phosphines and a phosphite. It was found that the combination of $P(OPh)_3$ and $Rh(acac)(CO)_2$ shows very high catalytic activity but poor regioselectivity. At 60°C under atmospheric pressure of a 1:1 mixture of CO and H_2 using a rhodium concentration of 10^{-3} M, and a P/Rh molar ratio of 10, a turnover frequency of 2.4 mol styrene conversion per mol rhodium min^{-1} was achieved. On the other hand, diphosphines are good cocatalysts, leading to 2-(*p*-methylphenyl)propanal in $> 90\%$ regioselectivity. The catalytic activity strongly depends on the P/Rh ratio, but the regioselectivity is not markedly affected by the P/Rh ratio [27].

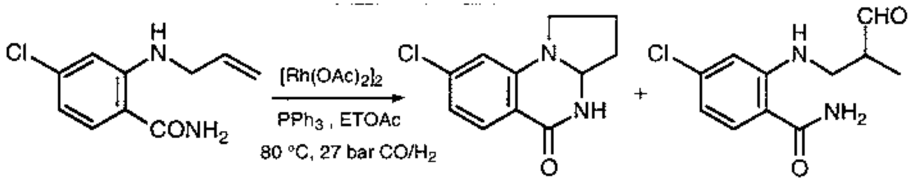
Hydroformylation of protected glucal derivatives **20** was studied by using rhodium catalysts. 2-Formyl derivatives were obtained as the main products in yields of 58%, 68%, and 55%, respectively, when $[Rh_2(\mu\text{-OMe})_2(COD)_2]/P(O\text{-}o\text{-}{}^tBuC_6H_4)_3$ was used as a catalyst precursor at 100°C and 50 bar $CO/H_2 = 1:1$ in dichloromethane [28].



(R = acetyl, benzyl, or methyl)

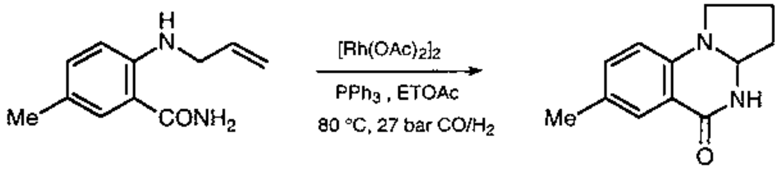
20

Rhodium-catalyzed reactions of 2-(allylamino)benzamides with 4-chloro, 5-methyl, and 5-nitro substituents in the arene ring gave varying yield of pyrrolo[1,2-a]quinazolines together with branched chain aldehydes [29].



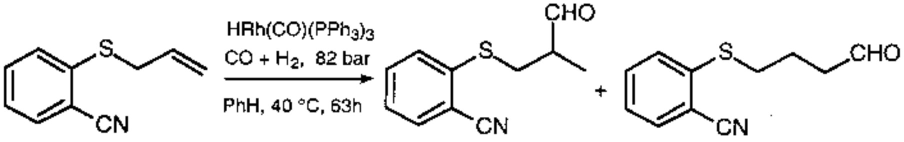
40 : 60

33% yield



99% isolated yield

Rhodium-catalyzed reactions of *o*-[(allyl and butenyl)thio] benzonitriles and benzamides 2-$RC_6H_4S(CH_2)_nCH{=}CH_2$ (R = cyano, $CONH_2$, $n = 1,2$) with CO/H_2 were found to give quantitative yields of the corresponding aldehydes. The results were compared with reactions of the analogous alkenylamines and alkenyloxy compounds [30], e.g.:



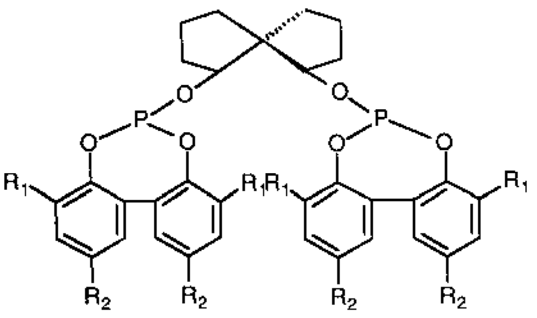
70 : 30

100% yield

Quaternary ammonium salts of phosphines as ligands were found to be useful in hydroformylation reactions. They offer special advantages for the catalyst separation using phase separation or membrane techniques [31]. High-melting phosphonium tosylates were used as solvents in the rhodium-catalyzed 1-hexene hydroformylation with and without added Ph_3P at 120°C and 40 bar $CO:H_2 = 1:1$. At the end of the reaction, the reaction mixture was cooled and the liquid organic product was separated from the solidified phosphonium tosylates which contained practically all of the rhodium-catalyst. These catalyst system could be reused several times and gave reproducible results [32].

Rhodium catalyst containing bidentate phosphines with natural bite angle being 102–113°, particularly DIOP, were found to be effective for 1,6-hexanedial formation in the hydroformylation of 1,3-butadiene. Thus, a mixture of 1,3-butadiene, $Rh_4(CO)_{12}$ ([Rh] = 0.1 mol%), and DIOP (DIOP/Rh = 5/1) at 90 bar of $CO/H_2 = 1/1$ in mesitylene as the solvent at 100°C gave after a 1.5 h reaction time 31% 1,6-hexanedial, 52% 3-pentenal, 8% 2-methyl-1,5-pentanedial, 1% 1-pentenal, and 0.2% 2-methyl-butanal [33].

High regioselectivities (97%) and high yields (98%) of 2-phenylpropanal were obtained under mild reaction conditions (25–40°C) in the rhodium-catalyzed hydroformylation of styrene modified by chiral diphosphite ligands **21**. Enantioselectivities up to 69% were achieved [34].



$R_1 = R_2 = H; {}^tBu$

$R_1 = {}^tBu, R_2 = OMe$

21

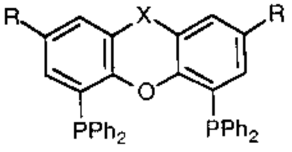
See also Refs. [37,38,42,47,48,50,53,60,62,76].

1.1.3. Other metals as catalysts and bimetallic catalysts

A comparison has shown that the complex *trans*-$[Ir(CO)(Ph_2PPy)_2Cl$ (py = pyridine) as a precursor in styrene hydroformylation at 80°C and 80 bar of $CO:H_2 = 1:1$ pressure is an order of magnitude more active than the Vaska complex *trans*-$[Ir(CO)(Ph_3P)_2Cl]$, making clear a favorable effect of the pendant Ph_2PPy ligand. At 56.2% conversion 46.1% hydrogenation and 43.9% hydroformylation was observed. The branched/linear ratio of the aldehydes is 91/9 [35].

Highly regioselective hydroformylation of methyl 3-pentenoate to linear 5-formyl methyl pentenoate was achieved by using the Pt/Sn catalyst system modified by diphosphine ligands. It was shown that activity as well as selectivity are controlled both by the bite angle and the rigidity of the backbone of the diphosphine ligand

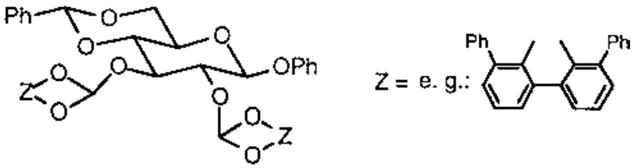
22. At 80°C and 10 bar $CO/H_2 = 1$ using **22b** and $PtCl_2 + SnCl_2$ as the catalyst precursor, linear to branched ratios higher than 90:10 were reached [36].



	X	R
a	H, H	H
b	$SiMe_2$	H
c	S	Me
d	^iPr	H

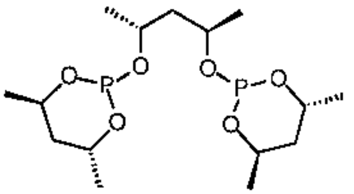
22

Rhodium(I) and platinum(IV) complexes of new carbohydrate bis-phosphites chiral ligands (**23**) were tested as catalysts for the asymmetric hydroformylation of vinyl acetate, allyl acetate and *p*-methoxy-styrene. Good regioselectivity (> 90% branched product) but an enantioselectivity of only ≤ 36% ee were found under mild reaction conditions (25–40°C, 40–70 bar $CO:H_2 = 1:1$) in the best case (allyl acetate, $[Rh(acac)(CO)_2]$) [37].

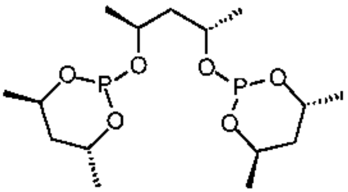


23

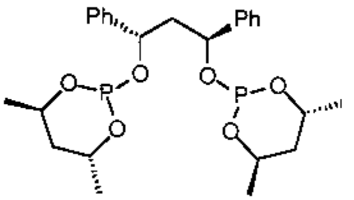
The chiral diphosphite ligands **24**–**27** were tested in rhodium- and platinum-catalyzed asymmetric hydroformylation of styrene. Both the rhodium and platinum complexes of the chiral diphosphite ligands were found to be active catalysts for the asymmetric hydroformylation of styrene but with moderate enantioselectivity. The highest enentioselectivity (40%) was obtained with the Platinum(II)–$SnCl_2$ catalytic system associated with **24** [38].



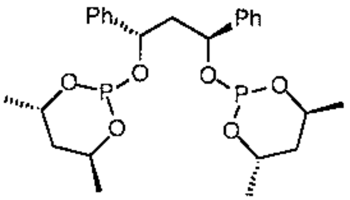
24



25

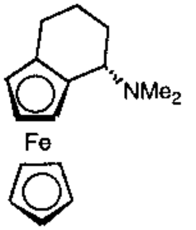


26

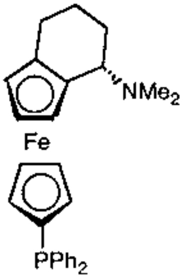


27

Both the 'preformed' and in situ $PtCl_2(L)$-type platinum catalysts (L = **28** and **29**) have been used in the enantioselective hydroformylation of styrene. In the best case at 80°C and 80 bar $CO:H_2 = 1:1$, a 21% enantiomeric excess of (*S*)-$PhCH(CH_3)CHO$ in the reaction product was observed [39].



28



29

See also Refs. [25,84].

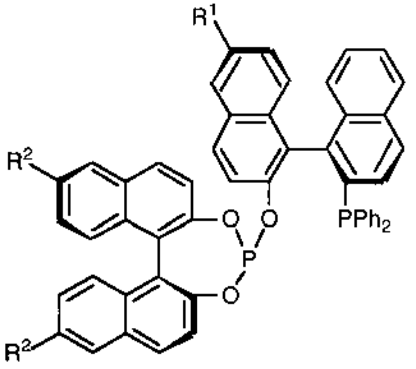
1.2. Heterogeneous systems

1.2.1. Supported complexes

The results of ethene hydroformylation at 173°C over a $Co(acac)_3/SiO_2$ catalyst showed that the catalyst activity was three times greater than a catalyst prepared by impregnation of cobalt nitrate. The oxo-selectivities of the two catalysts were similar. The higher activity of the $Co(acac)_3/SiO_2$ catalyst was explained by the presence of highly dispersed active sites in this catalyst favoring carbon monoxide insertion [40]. Octakis-(tetracarbonylcobaltio)octasilsesquioxane $[Co(CO)_4]_8Si_8O_{12}$ in combination with triphenylphosphine in a 1:8 stoichiometry was found to show catalytic activity in the hydroformylation of 1-hexene. At 120°C and 70 bar $CO:H_2 = 1:1$ pressure 98% yield of the corresponding aldehydes were obtained as a 3:1 mixture of 1-heptanal and 2-methylhexanal [41].

According to the results of IR characterization and catalytic study in ethylene hydroformylation, the reaction of $Co_2(CO)_8$ with $[Rh(CO)_2Cl]_2$ (Rh:Co = 1:3 atomic ratio) on the surface of SiO_2 rapidly gives $RhCo_3(CO)_{12}$. The same bimetallic cluster was obtained from $Co_4(CO)_{12}$ and $[Rh(CO)_2Cl]_2$ (Rh:Co = 1:3 atomic ratio) on the surface of SiO_2 under reducing conditions [42].

Asymmetric hydroformylation of olefins using polymer-immobilized chiral phosphine-phosphite-rhodium(I) complexes has been studied. The polymer-support of the Rh(acac)-catalyst was a highly crosslinked polymer obtained from a radical copolymerization of vinyl-BINAPHOS **30** with divinylbenzene. Asymmetric hydroformylation of styrene using this polymer-ligand-Rh(acac) complex at 60°C in benzene at 20 bar and 100 bar total pressure of $CO:H_2 = 1:1$, gave a quantitative conversion to aldehydes. Thus, with polymeric-**30a**-Rh(acac), 2-phenylpropanal and 3-phenylpropanal were obtained in a 84:16 ratio and the enantiomeric excess of the *iso*-aldehyde was 89% (*R*). The same result was obtained when the catalyst was prepared by the copolymerization of divinylbenzenes with the Rh(acac)-complex of **30a**. Asymmetric hydroformylation of vinyl acetate at 100 bar total pressure using the polymer supported catalysts gave an iso/normal-ratio of 85:15 to 90:10 and 89–93% ee (*S*), similar to those obtained in the homogeneous system [43].



a) R^1 = -CH=CH$_2$, R^2 = H

b) R^1 = H, R^2 = -CH=CH$_2$

c) R^1 = -CH=CH$_2$, R^2 = -CH=CH$_2$

30

Silica-tethered rhodium thiolate catalysts prepared by the condensation of $[Rh_2[\mu\text{-}S(CH_2)_3Si(OCH_3)_3]_2(CO)_4$ or $[Rh_2[\mu\text{-}S(CH_2)_3Si(OCH_3)_3]_2[Ph_2P(CH_2)_3Si{-}(OC_2H_5)_3]_2\text{-}(CO)_2$ on silica gel were found to exhibit high activity for hydroformylation of 1-octene in the presence of phosphine or phosphite ligands under the mild conditions of 60°C and 1 bar total pressure of H_2 and CO. The catalysts are easily separated from the reaction mixtures. In the best case the catalyst maintains its activity through at least three cycles over a total period of 69 h, during which time there are 1273 mol of aldehyde/mol of rhodium turnovers. In all experiments, the hydroformylation products were 1-nonanal and 2-methyloctanal. Effects of the phosphine ligand and phosphine/rhodium mole ratio on the hydroformylation rate, conversion, and chemo- and regioselectivity for aldehyde products were also investigated [44].

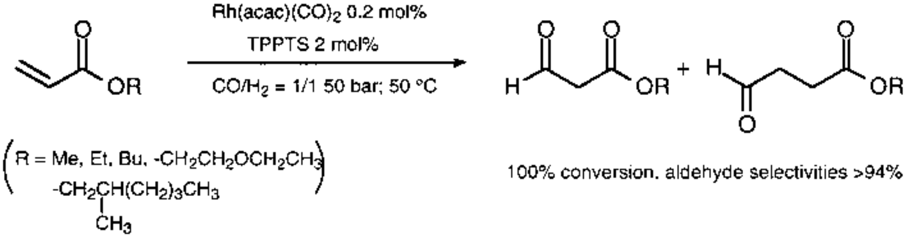
A SiO_2-supported rhodium-phosphine complex catalyst for hydroformylation of propene was studied by using $^{31}P(^1H)$-NMR spectroscopy. The experimental results showed that, after the $HRh(CO)(PPh_3)_3$ complex was supported on SiO_2, the original characteristic ^{31}P-NMR signal at 41.1 ppm for this complex in benzene disappeared and a new broad signal appeared at 37.0 ppm, which originated most probably from the interaction between the supported rhodium-phosphine complex and the surface of SiO_2 carrier. The NMR spectrum of the functioning catalyst after 4h at propene hydroformylation operation revealed that the dominant species of rhodium–phosphine at the surface were the intermediates containing two carbonyl ligands or a carbonyl and an acyl ligand [45].

1.2.2 Biphasic systems

Hydroformylation of ethylene and propylene using a water-soluble and air-stable ruthenium complex $Ru_3(CO)_9(TPPMS)_3$ (TPPMS = sodium-*m*-(diphenylphosphino)benzenesulfonate) was studied [46].

The kinetics of hydroformylation of ethylene was studied using $HRh(CO)(PPh_3)_3$ and $[Rh(COD)Cl]_2$/TPPTS (TPPTS = trisodium tris(*m*-sulfonatophenyl)phosphine) catalyst in toluene and water media, respectively. The rates were found to have a first-order dependence on the catalyst concentration. A comparison of the organic and aqueous systems have shown that there are similar trends with respect to partial pressures of ethylene and carbon monoxide in both solvents. The major difference observed was a 1.5 order with dihydrogen in toluene compared with a first order in water [47].

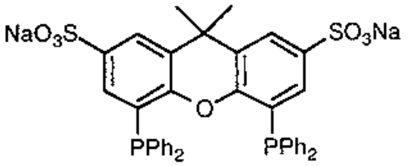
Rate enhancement by a factor of 2–14 was observed in hydroformylation of various acrylic esters, relatively soluble in water, in a two-phase system using water-soluble rhodium complex of trisulfonated triphenylphosphine as the catalyst compared to those in a homogeneous single-phase system. Regioselectivity of both homogeneous and biphasic systems was almost exclusively directed towards the formation of the branched aldehyde [48].



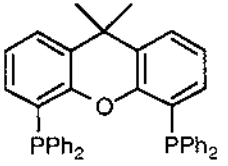
100% conversion, aldehyde selectivities >94%

The kinetics of biphasic hydroformylation of 1-hexene using a water-soluble rhodium–tristriphenylphosphino trisulfonate complex catalyst with ethylene glycol as a co-solvent were investigated. The effects of partial pressure of CO, partial pressure of dihydrogen, and olefin concentration on the activity were studied at 80°C [49].

The new water-soluble catalyst system derived from **31** and $Rh(acac)(CO)_2$ was found to be catalytically active in the two-phase hydroformylation of alkenes and shows high regioselectivity for the linear aldehyde in the case of propene and 1-hexene. Thus, at 120°C, $P = 9$ bar propene and 10 bar $CO/H_2 = 1/1$ 97.5% *n*-butyraldehyde was obtained, which is similar to that obtained using **32** as ligand in non aqueous solvents [50].

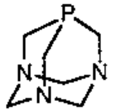


31

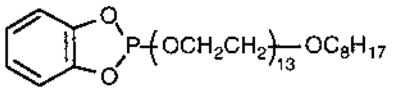


32

Catalytic activity of rhodium(I) complexes Rh(acac)(CO)(L) with L = **33**, $P(CH_2CH_2CN)_3$, and tris(3-sodium sulfonatophenyl)phosphine for hydroformylation of 1-hexene in a two-phase system has been tested. At 30 bar $CO:H_2 = 1:1$ and 60°C the initial rate of the reaction was found to be 61, 111, and 109 mol/h × mol × Rh, respectively [51].



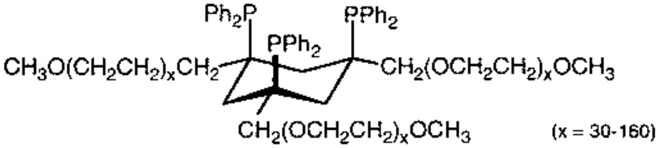
33



34

The two-phase hydroformylation of styrene using the $Rh(acac)(CO)_2$ + water-soluble nonionic octyl–polyglycol–phenylene–phosphite **34** catalyst system was investigated. At 80°C and 50 bar ($CO:H_2 = 1:1$) up to 99.6% conversion and up to 99.3% aldehyde yield was observed with a molar ratio of branched/linear aldehyde ratio of 4.8 [52].

The catalytic activity of the rhodium complex with the water-soluble tripodal phosphine ligand **35** in the hydroformylation of 1-hexene was found to be comparable in a single-phase (1-hexene/methanol) with that in the biphasic system (1-hexene/water) [53].

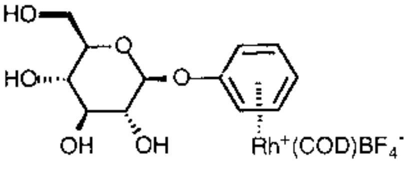


35

Mono- and di-*p*-polyoxyethylene substituted triphenylphosphines combined with rhodium(III) chloride were found to be good catalysts in the aqueous/organic biphasic hydroformylation of 1-hexene. With a conversion up to 95%, the catalyst can be reused five times without loss in activity. The ligands possess inverse temperature-dependent solubility in water, and therefore the catalyst transfers into the organic phase to catalyze the reaction at a higher temperature, and returns to the aqueous phase to be separated from the product at lower temperature, after the reaction is completed [54].

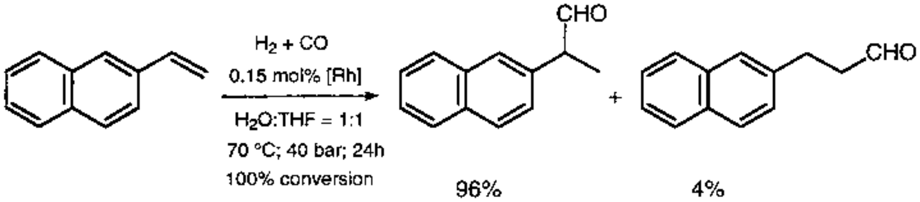
The catalytic activity of new rhodium systems formed in reactions of catalyst precursor $[Rh(acac)(CO)_2]$ with the water-soluble phosphines: $Ph_2PCH_2CH_2CONHC(CH_3)_2CH_2SO_3Li$, $Ph_2PCH_2CH(COOLi)$, $Ph_2PCH_2CH(CH_3)COOH$, and $Ph_2PCH_2CH(CH_3)(COONa)$ was studied in hydrogenation and hydroformylation of 1-hexene under mono- and biphasic conditions [55].

A water-soluble rhodium complex **36** was used as a catalyst precursor for the hydroformylation of olefins in a two-phase (water and hexane) system. Under optimized reaction conditions (40°C, 30 bar $H_2:CO = 2:1$, 5 mol% Rh, 22 h) styrene and substituted styrenes gave a 100% yield of the predominantly branched aldehyde. 1-Heptene and 1-octene led to a 44/56 ratio of the corresponding branched and linear aldehydes [56].



36

A water-soluble complex Rh/PPA(Na^+)/DPPEA (PPA = poly(4-pentenoic acid; DPPEA = bis[2-(diphenylphosphino)ethyl]amine) was found to be a highly active catalyst for the hydroformylation of olefins. High ratios of branched aldehydes were observed in the case of vinyl ethers at 40 bar ($CO/H_2 = 1$) and 90°C, and in the case of vinyl arenes at 40 bar ($CO/H_2 = 1$) and 70°C [57], e.g.:



Several ways to increase the efficiency in the $[Rh_2(\mu\text{-S}^t\text{Bu})_2(CO)_2(TPPTS)_2]$-catalyzed hydroformylation of heavy alkenes was investigated. For example b-cyclodextrin was used as a phase-transfer agent allowing the inclusion of the substrate and its transport to the aqueous phase where the reaction is occurring [58].

The two-phase hydroformylation of 1,3-butadiene using $HRh(CO)[P(m\text{-}C_6H_4SO_3Na)_3]_3$ and excess $P(m\text{-}C_6H_4SO_3Na)_3$ as the catalyst was found to give high yields (up to 84%) of C_5 monoaldehydes in water-diethylether at 110°C and 60 bar CO/H_2. The main product in this mixture is *trans*- and *cis*-pent-3-enal, which might be the starting material for 2-propylheptanol-1, a plasticizer alcohol with better ecological properties than 2-ethylhexanol-1 [59].

Catalytic hydroformylation of unsaturated carbohydrates (glucals) to give the dimethyl acetal of 2-C-formyl-D-alditol derivatives was studied using the catalytic system $[Rh(\mu\text{-OMe})(COD)]_2/P(O\text{-}o\text{-}^tBuC_6H_4)_3$/PPTS (PPTS = pyridinium-*p*-toluenesulfonate). It was found that at 100°C and 50 bar $CO{:}H_2 = 1{:}1$ pressure the yields are strongly dependent on the protecting groups on the carbohydrate [60].

Advances in the hydroformylation of propene via homogeneous catalysis for the manufacture of *n*-butanal using rhodium-tris(triphenylphosphine sulfonate) as the catalyst were discussed in the context of the Ruhrchemie/Rhone–Poulenc process. The easy separation of catalyst and product is emphasized as the main advantage of the two-phase catalyst system [61].

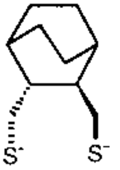
A detailed study of the fluorous-soluble $Rh/P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst system for the hydroformylation of both low and high molecular weight olefins (ethylene and decene-1) at 110 or 100°C and 11 bar CO/H_2 (1:1) in a 50/50 vol.% toluene/perfluoromethylcyclohexane solvent mixture was reported. The liquid phase of this system is homogeneous at and above 100°C but forms two-phases at lower temperatures which allows the facile separation of the aldehyde products from the fluorous catalyst. During nine consecutive reaction/separation cycles in the semi-continous hydroformylation of decene-1 with Rh/$P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst, a total turnover of more than 35 000 was achieved with a loss of 1.18 ppm rhodium/mol of undecanals. High-pressure NMR has revealed that under 21–83 bar of $CO:H_2 = 1:1$ an equilibrium between $HRh(CO)\{P[CH_2CH_2(CF_2)_5CF_3]_3\}_3$ and $HRh(CO)_2\{P[CH_2CH_2(CF_2)_5CF_3]_3\}_2$ does exist. Kinetic studies of the decene-1 hydroformylation showed that the reaction is first order in both rhodium and decene-1. The reaction is inhibited by $P[CH_2CH_2(CF_2)_5CF_3]_3$, and the normal/iso ratio of the aldehyde increases with increasing phosphine concentration. The catalytic activity of the Rh/$P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst was found to be similar to that of the nonfluorous analog Rh/$P[(CH_2)_7CH_3]_3$ catalyst and is an order of magnitude lower than that of the Rh/PPh_3 catalyst [62]. See also Ref. [24].

1.3. Coordination chemistry related to hydroformylation

A critical review of the existing data on the equilibrium reaction of dicobalt octacarbonyl with dihydrogen, along with the results of new infrared spectroscopic measurements under semi in-situ conditions has been published. The equilibrium constant, $K_p = [HCo(CO)_4]^2/[Co_2(CO)_8]\cdot P(H_2)$ (mol $l^{-1}\cdot$bar), obtained from these latter measurements in hexane as solvent, depends on temperature in the 50.7–117.0°C range according to the equation $\log K_p = -(0.670 \pm 0.106) - (886 \pm 38)/T$. The van't Hoff plot of these data yielded the thermodynamic parameters $\Delta H = 4.054 \pm 0.175$ kcal mol^{-1} and $\Delta S = 3.067 \pm 0.488$ cal mol$^{-1}\cdot$K [63].

Fluxional processes in the asymmetric hydroformylation catalyst $HRh(L-L)(CO)_2$ (L–L = C_2-symmetric diphosphite ligands) have been investigated by variable-temperature ^{31}P- and ^{1}H-NMR spectroscopy [64].

The solution structures of the dominant species present during the asymmetric styrene hydroformylation using precursors $[Rh(\mu\text{-}OMe)(COD)]_2$ and the dithiolate-bridged complex $[Rh_2(\mu\text{-}\mathbf{37})(COD)_2]_2$ in the presence of BDPP was determined by high-pressure NMR and IR spectroscopy. The mononuclear complex $[HRh(BDPP)(CO)_2]$ is proposed to be the predominant species during the hydroformylation process, but the dimeric species $[Rh(BDPP)(CO)_2]_2$ is also present and in equilibrium with the mononuclear complex [65].



37

Intermediate hydrido-, alkyl- and acyl-complexes of platinum-diphosphine (BDPP and dppp) hydroformylation catalysts were identified using high pressure NMR [66].

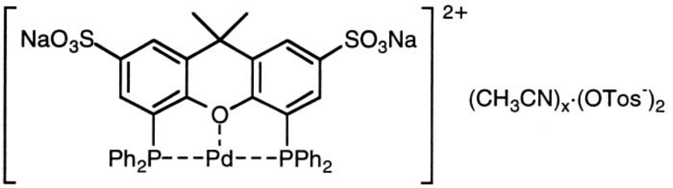
2. Hydroformylation related reactions of CO

2.1. *Silylformylation, homologation, hydrocarboxylation, alkoxycarbonylation, amidocarbonylation, hydroaminomethylation, thiocarbonylation and ketonformation*

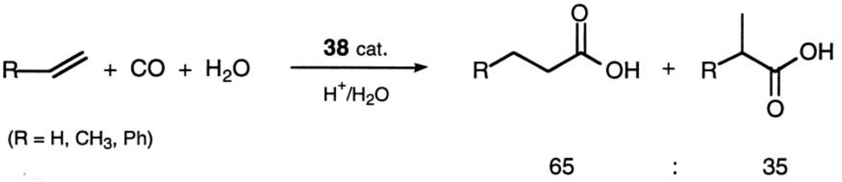
Possible mechanisms for the silylformylation of 1-alkynes catalyzed by $Rh_2Co_2(CO)_{12}$ were studied. Novel rhodium-cobalt mixed metal complexes $(PhMe_2Si)_2Rh(CO)_nCo(CO)_4$ ($n = 2$ or 3) and $[(CO)_2Co(\mu\text{-}CO)(\mu - HC{\equiv}CBu)Rh(CO)_2]$ were found to play roles in this catalysis. The reaction of the former complex with 1-hexyne and $HSiMe_2Ph$ at ambient temperature and pressure of CO gives ^{n}BuC(CHO)=CHSiMe$_2$Ph ($Z/E = 95/5$), $(PhMe_2Si)_2Rh(CO)_3Co(CO)_4$, and $Rh_2Co_2(HC{\equiv}C^nBu)(CO)_{10}$. The reaction of $[(CO)_2Co(\mu\text{-}CO)(\mu\text{-}HC{\equiv}CBu)Rh(CO)_2]$ with 1-hexyne and $HSiMe_2Ph$ under the same ambient conditions affords Z-BuC(-CHO)=CHSiMe$_2$Ph cleanly as the sole reaction product. The crossover experiments using $RhCo(DC{\equiv}CBu)(CO)_5$, 1-hexyne-1d and $DSiMe_2Ph$ strongly support the mixed metal bimetallic catalysis, and involvement of bis(alkyne)rhodium-cobalt species [67].

The manganese(salen)Cl_2 complex (salen = N,N'-ethylenebis(salicylideneamidato)) encapsulated in Zeolite-Y 2 was found to catalyze the homologation of methanol in the presence of carbon monoxide and an iodide promoter at 30 bar and 150°C to give dimethylether and acetic acid as the main products [68]. The hydrocarbonylation of acetic acid into higher homologues was investigated at 200 bar and 220°C by using rhodium/iodide systems. In homogeneous catalysis the most convenient precursor proved to be $[RhI_2(CO)_2]^-$ prepared from $[RhCl(CO)_2]_2$ in the presence of LiI. Mean turnover frequencies of 67 h^{-1} and selectivities as high as 80% in propionic acid were obtained [69].

A highly selective water-soluble dicationic palladium catalyst **38** has been used for the biphasic hydrocarboxylation of alkenes. Under optimized reaction conditions (30 bar, 120°C, 2.7 mol p-$CH_3C_6H_4SO_3H$/mol olefin), no formation of metallic palladium was observed and initial turnover frequencies dropped only slightly within hours indicating that the system is stable under the reaction conditions [70].



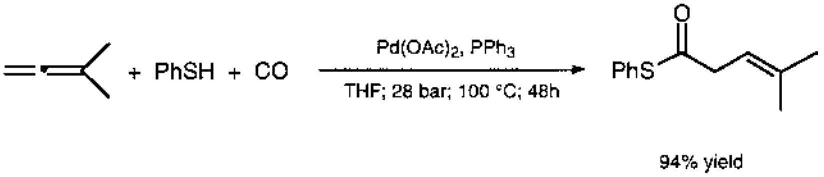
38



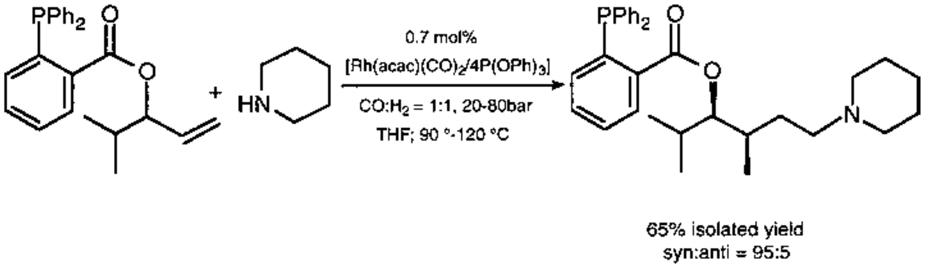
A poly(*N*-vinyl-2-pyrrolidone)-supported $PdCl_2$–$NiCl_2$–PPh_3 bimetallic system was found to be an efficient catalyst for the hydroesterification of styrene with CO and methanol. This catalyst provides a highly regiospecific hydroesterification to the branched acid ester with complete conversion at 80°C and 210 bar carbon monoxide pressure [71]. The asymmetric hydroesterification of norbornene catalyzed by a palladium acetate, 1,4:3,6-dianhydro-2,5-bis(diphenylphosphino)-L-iditol and *p*-toluenesulfonic acid catalytic system was studied using mild reaction conditions. Optical yield up to 92.2% and chemical yield of 71.6% are obtained under 50 bar, 120°C and a molar ratio of P:Pd = 1 [72].

A detailed investigation of the palladium-catalyzed amidocarbonylation has led to a highly efficient process with the active catalyst system $PdBr_2/2PPh_3/LiBr/H_2SO_4$. Using this catalytic system and various aldehydes and acetals as starting materials gave the corresponding *N*-acyl amino acids in 85–95% isolated yield at 120°C and 60 bar carbon monoxide pressure in *N*-methyl-pyrrolidone solution. Based on the study of the influence of solvent, temperature, pressure, co-catalysts and substrates a mechanism of the palladium-catalyzed amidocarbonylation was suggested [73].

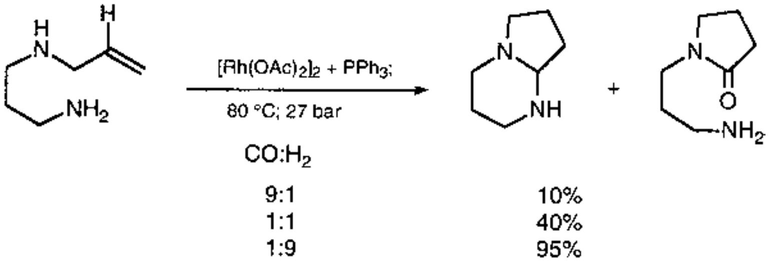
Palladium catalyst systems such as $Pd(OAc)_2/PPh_3$ have been found to catalyze the carbonylative addition of thiols and carbon monoxide to allenes, leading to the regioselective formation of α,β-unsaturated thioesters [74], e.g.:



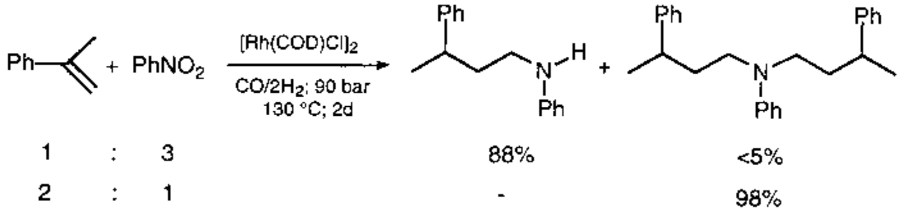
Substrate directed diastereoselective hydroaminomethylation of methallylic alcohols has been achieved with the aid of the substrate bound catalyst directing *o*-diphenylphosphinylbenzoate group. The amines were obtained in fair to good yields in diastereomer ratios ≥ 94:6 (*syn*:*anti*). The anticipated mechanism of this sequential transformation involves presumably three steps. First the hydroformylation of the substrate provides the aldehyde which react with the secondary (or primary) amine, giving rise to the formation of the corresponding enamine (or imine). Rhodium-catalyzed hydrogenation finishes the sequence of reactions and affords the saturated amine products [75].



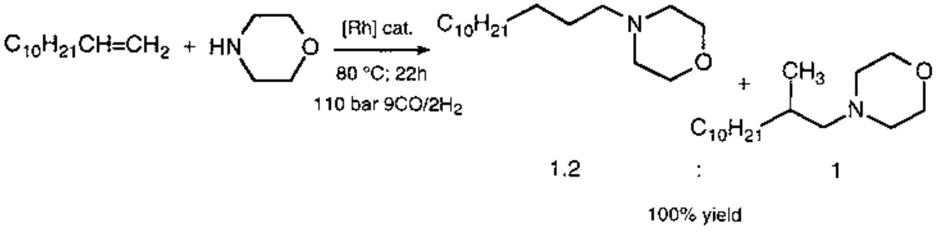
The rhodium-catalyzed reaction of *N*-alkenyl-1,3-diaminopropanes with CO/H_2 was found to give usually mixtures of diazabicycloalkanes and aminopropyl laktames. The chemoselectivity and regioselectivity of these reactions are influenced by the choice of ligand and by the ratio of H_2 and CO in the gas mixture [76], e.g.:

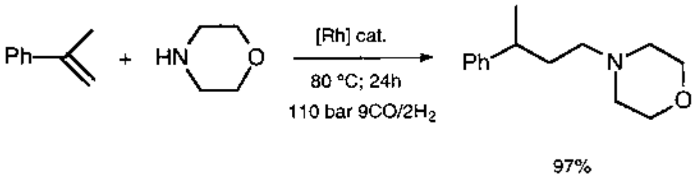


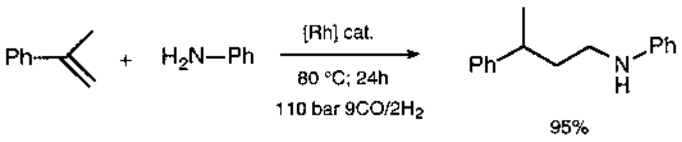
Secondary and tertiary amines were selectively prepared in high yields under hydroformylation conditions by a one-pot reduction/multiple alkylation procedure from aromatic nitro compounds with styrenes, cyclic olefins or hetero-functionalized olefins, carbon monoxide and dihydrogen in the presence of 1 mol% {Rh(COD)Cl]$_2$ as the catalyst precursor [77], e.g.:

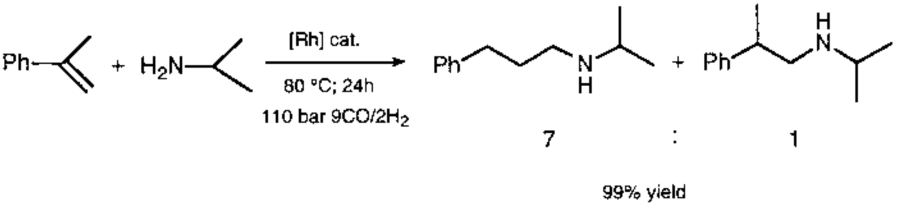


Secondary and tertiary amines were selectively prepared in high yields by the reaction of alkenes with primary or secondary amines, carbon monoxide and dihydrogen in the presence of 1 mol% [Rh(COD)Cl]$_2$ as a catalyst precursor via a one-pot hydroformylation-amine condensation-reduction sequence [78], e.g.:

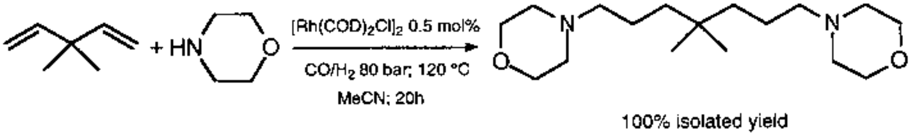


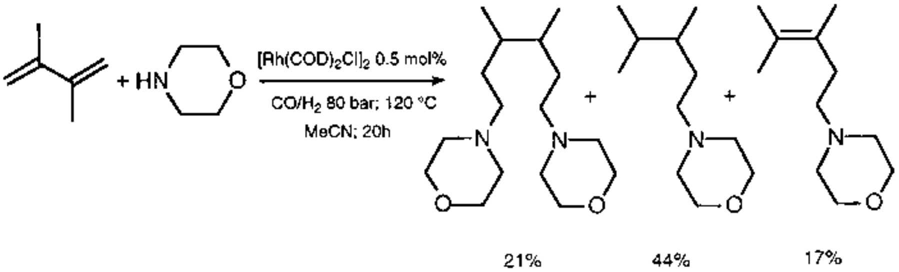




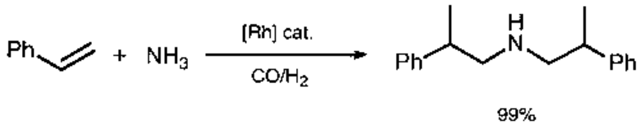


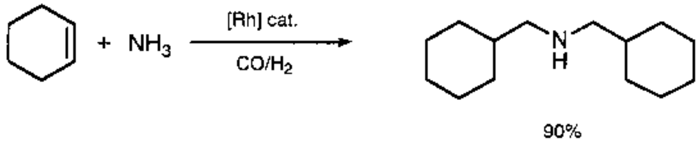
Bis(hydroaminomethylation) of nonconjugated α,ω-diolefins with secondary amines leads to tertiary α,ω-diamines in good to excellent yields. Conjugated diolefins, such as 2,3-dimethyl-1,3-butadiene, give a mixture of diamine products [79], e.g.:

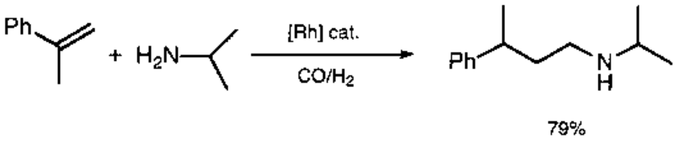


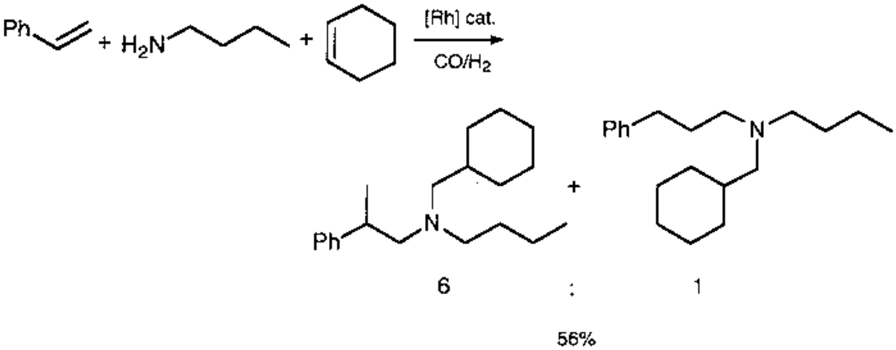


Using ammonia or primary amines with styrenes and/or cyclic olefins, the one-pot synthesis leads to symmetrically and substituted amines [80], e.g.:

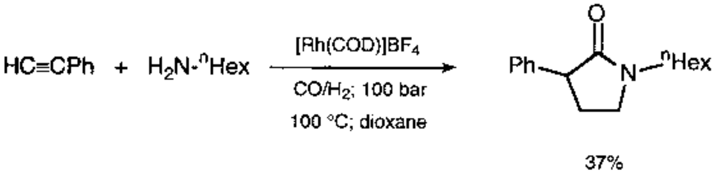


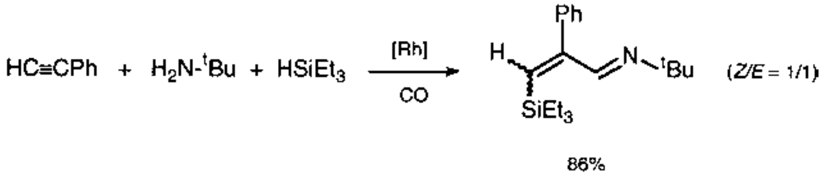






In a one-pot rhodium(I)-catalyzed hydroaminomethylation procedure, alkynes in the presence of primary amines give substituted 2-pyrrolidinones. Replacement of dihydrogen by hydrosilanes via silylcarbonylation was found to lead to 4-silylated 1-aza-1,3-butadienes [81], e.g.:





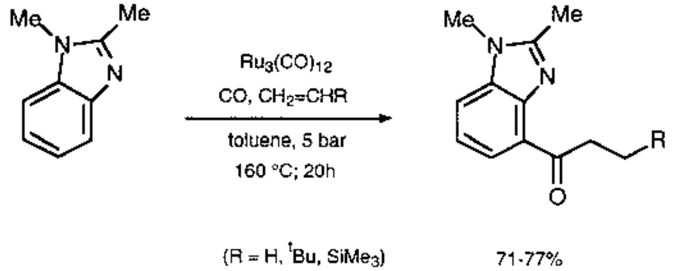
The complex $Ph(Et)_2N{\cdot}BH_3$ and anhydrous $CoCl_2$ in the presence of carbon monoxide was found to be a useful reagent for the hydroboration and carbonylation of alkenes to obtain the corresponding dialkyl ketones in 50–70% isolated yield after oxidation with H_2O_2/NaOH [82].

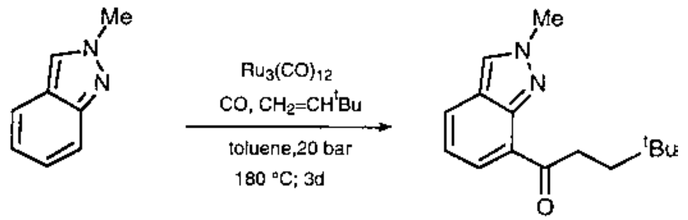
$$CoCl_2 \xrightarrow[\substack{\text{CO, 1 bar} \\ 25°\text{C, 2 h}}]{PhEt_2N \cdot BH_3} \xrightarrow[\text{CO, 1 bar; 5 − 6h}]{RCH{=}CH_2} \xrightarrow[25°\text{C}]{36\text{ h}} \xrightarrow[\text{NaOH}]{H_2O_2} RCH_2CH_2CCH_2CH_2R$$

$$+ RCH_2CH_2OH$$

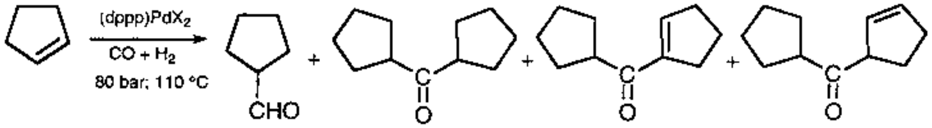
where R = n-$C_{10}H_{21}$; n-C_4H_9; $H_3CO_2C(CH_2)_8$; c-C_6H_{11}; c-C_5H_9.

Aza-heterocycles were selectively carbonylated at the C–H bond β to the nitrogen in the presence of olefins and $Ru_3(CO)_{12}$ at 160–180°C and 5–20 bar carbon monoxide pressure to form the corresponding ketone [83], e.g.:





The selectivity for ketones **39**, **40**, and **41** in the (dppp)PdX_2-catalyzed hydrocarbonylation of cyclopentene was found to increase from 14 to 98% reflecting the decrease in coordination strength of the anionic ligands in the series of (dppp)PdX_2 complexes X = TFA, OMs, OTos, OTf [84]. See also Refs. [25,29].



39 **40** **41**

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

The homogeneous catalytic water gas shift reaction by solutions of $Re_2(CO)_{10}$ in aqueous pyridine or other substituted pyridine solutions was studied at [Re] = 10 mM, $P(CO) = 0.9$ bar and $T = 100$ °C. The best results showed the following order of reactivity, expressed as turnover frequencies of dihydrogen production, defined as moles of H_2/mol Re/day: 4-picoline{9.5} > pyridine{6.8} > 2-picoline{1.0} [85].

Kinetics of the water gas shift reaction catalyzed by *cis*-$[Ir(CO)_2(4\text{-picoline})_2]PF_6$ in aqueous 4-picoline was studied. The catalytic activity proved to be nonlinear in iridium total concentration over the range 5 to 80 mM, which was interpreted in terms of the presence of active mononuclear and polynuclear iridium species in the system, being the mononuclear the more active. The rate was found to be first order on CO pressure over the range of 0.7 to 1.9 bar. This result was interpreted by the assumption that the CO addition to the catalytic species is prior to the rate-limiting step [86].

Azamacrocyclic derivatives of $H_4Ru_4(CO)_{12}$ $[LH]^+[H_3Ru_4(CO)_{12}]^-$ (L = 1,4,7-triazacyclononane, 1,4,7-trimethyl-1,4,7-triazacyclononane, 1,5,9-triazacyclo-dodecane, and 1,5,9-trimethyl-1,5,9-triazacyclododecane) were studied in the water gas shift reaction at 0.4–0.6 bar carbon monoxide pressure at 170°C. In the best case using the complex $[H_3Ru_4(CO)_{12}][H(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})]$ as the catalyst, 13.31 mol H_2/ mol Ru/day activity was observed under the above conditions [87].

Activation of silica-supported ruthenium mono(bipyridine) carbonyls $[Ru(bpy)(CO)_2Cl_2]$, $[Ru(bpy)(CO)_2ClH]$, $[Ru(bpy)(CO)_2Cl(C(=O)OCH_3)]$ or $[\{Ru(bpy)(CO)_2Cl\}_2]$ with dilute NaOH or KOH solution results in highly active water-gas shift catalysts. The highest activities were obtained with NaOH treated $[\{Ru(bpy)(CO)_2Cl\}_2]/SiO_2$, which gave turnover frequencies as high as 14 500 mol CO_2/mol Ru/day at 150°C [88].

The heterogenized water gas shift catalyst Rh/P4VP, prepared from the reaction of rhodium(III) chloride with poly(4-vinylpyridine) (P4VP) was found to be active for hydrogenation and hydroformylation of 1-hexene and cyclohexene in aqueous ethoxyethanol under mild shift reaction conditions (0.9 bar $P(CO)$ at 100°C). Hydroformylation rates increased with increasing partial pressure of carbon monoxide, but exhibited saturation behavior in the 1.5 bar range. Cyclohexene hydroformylation turnover frequencies were found to be independent of the polymer loading [89].

Homogeneous catalytic reduction of nitrobenzene to aniline by *cis*-$[Rh(CO)_2(amine)_2]PF_6$ (amine = 4-picoline, 3-picoline, 2-picoline, pyridine, 3,5-lutidine, 2,6-lutidine) in aqueous amine solution (2/8 = vol./vol.), 0.9 bar carbon monoxide partial pressure at 100°C under water gas shift reaction conditions is described. The effect of various amines as additives was investigated [90].

Thermostable robust platinum clusters $[Pt_{15}(CO)_{30}]^{2-}$ combined with R_4N^+ (R = Me, Et, Bu, and Hex) and MV^{2+} encapsulated in the ordered hexagonal mesoporous channels of FSM-16 (27.5 Å diameter) show remarkably higher catalytic activities for the water gas shift reaction, compared with $[Pt_9(CO)_{18}]^{2-}$ and $[Pt_{12}(CO)_{24}]^{2-}$ clusters restricted in NaY micropores (12 Å) [91].

Homogeneous catalysis of the water gas shift reaction has been accomplished by the use of solutions of $CuCl_2{\cdot}2H_2O$ in aqueous pyridine and other substituted pyridine solutions. Turnover frequencies for dihydrogen production were found to be of about 6 mol H_2/mol Cu/day for [Cu] = 20 mM, $P(CO) = 1.9$ bar and $T = 120$°C [92]. See also Ref. [77].

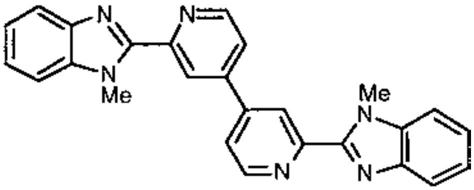
2.3. Reduction of CO and CO_2

The surface hydrogenation of carbon monoxide on a ZrO_2-supported ruthenium–iron catalyst using $Ru_3(CO)_{12}$–$Fe_2(CO)_9$ cluster precursors was studied by in situ IR spectroscopy. According to some C–H stretching frequencies methyl and methylene surface species were inferred [93].

Heating solutions of $[(\eta^5:\eta^1\text{-}C_5H_4(CH_2)_nNMe_2)Ru(dppm)]BF_4$ under H_2/CO (40 bar/40 bar) at 80°C for 16h gave formic acid in low yields ($n = 2$; TON = 6; $n = 3$; TON = 8). The formation of formic acid was explained by a mechanism involving intramolecular heterolytic cleavage of the bound dihydrogen to generate $[(\eta^5\text{-}C_5H_4(CH_2)_nNMe_2H^+)RuH(dppm)]BF_4$, followed by CO_2 insertion into the Ru–H bond and then N–H protonation of the formate ligand [94].

Equilibrium mixtures of phosphine-substituted ruthenium carbonyl carboxylates under dihydrogen pressure were found to catalyze the reduction of carbon monoxide to carbon monoxide and water [95].

Electrochemical reduction of carbon dioxide catalyzed by mono- and dinuclear ruthenium complexes such as $[(bpy)_2Ru(\mathbf{42})][PF_6]_2$ and $[(bpy)_2Ru(\mathbf{42})(bpy)_2][PF_6]_4$ produced formic acid selectively with only trace amounts of carbon monoxide and oxalate-ion in the presence and absence of water, respectively, in acetonitrile [96].

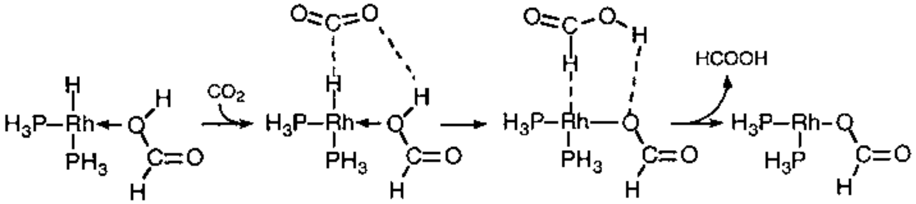


42

The cyclic voltammogram of the ruthenium complex *trans*-Cl_2-$[RuCl_2L(CO)]$ (L = 6-(2-diphenylphosphinoethyl)-2,2′-bipyridine)) shows one irreversible system at $E_{pc} = -1.71$ V and two reversible system at $E_{1/2} = -1.86$ and -1.91 V. In the presence of carbon dioxide the latter redox system exhibits a pronounced electrocatalytic current, resulting in the formation of carbon monoxide [97].

One-electron reduction of cobalt(I) porphyrin was found to lead to formation of a cobalt(0) porphyrin species which binds and reduces carbon dioxide. Catalytic formation of carbon monoxide and HCO_2^- was confirmed by photochemical experiments in acetonitrile solutions containing triethylamine as a reductive quencher. Catalytic reduction of carbon dioxide was also confirmed by cyclic voltametry in acetonitrile at the potential at which cobalt(I) porphyrin is reduced to cobalt(0) porphyrin [98].

Density functional methods has been applied to investigate the release of HCOOH from the $[(PH_3)_2(H)Rh(HCOOH)]$ complex in the last step of the hydrogenation of carbon dioxide catalyzed by rhodium complexes. It was found that the presence of a CO_2 molecule in the model of the active site favors the thermodynamics of the HCOOH dissociation from the $[(PH_3)_2(H)Rh(HCOOH)]$ species [99].



Infrared spectroelectrochemical and electrochemical kinetics studies of the reaction of nickel cluster radicals $[Ni_3(\mu_2\text{-dppm})_3(\mu_3\text{-L})(\mu_3\text{-I})$ (L = CNR, R = Me, ^{i}Pr, ^{c}Hex, $PhCH_2$, ^{t}Bu, $2,6\text{-}Me_2C_6H_3$; L = CO) with carbon dioxide have been made. Electrochemical kinetic studies indicate that the rates of reaction with CO_2 depend to first order on the cluster concentration and to the first order on CO_2 concentration. Based on the kinetic and spectroscopic results, a mechanism for the catalytic reduction of CO_2 involving CO_2 activation on the isocyanide-capped face of the trinuclear nickel cluster is proposed [100]. A single nickel system in form of the complex $(P^cHex_3)_2Ni(CO)_2$ was found which promote both the reduction of carbon dioxide to carbon monoxide and the subsequent coupling of carbon monoxide with an olefin and a thio group to afford an organic thioester, mimicking the carbon monoxide dehydrogenase enzyme activity [101].

Ab initio MO/MP2 and MP4SDQ calculations have shown that the insertion of carbon monoxide into the Rh–H bond of *cis*-$[RhH_2(PH_3)_3]^+$ and *cis*-$[RhH_2(PH_3)_2(H_2O)]^+$ requires a very high activation barrier of 54 kcal/mol when the hydride ligand is *trans* to carbon monoxide, but an activation barrier of 44 kcal/mol when the PH_3 ligand is *trans* to carbon monoxide, and a moderate barrier of 24 kcal/mol when H_2O is *trans* to carbon monoxide [102].

3. Reviews

1. Design of high-function catalyst material. A review with 19 references on the mechanisms in preparation of 1-propanol from synthesis gas, in preparation of alcohols by Fischer–Tropsch reaction and olefin hydroformylation [103].
2. Methods for manufacturing isobutyraldehyde A review with 20 references among others about the hydroformylation of propene using the supported aqueous-phase rhodium catalyst [104].
3. Industrial aqueous biphasic catalysis: status and directions. A review with 40 references [105].
4. Technological development of hydroformylation in aqueous and organic phases. A review with 13 references. [106].
5. The fluorous biphase concept which was successfully applied among others in 1-decene hydroformylation using $HRh(CO)(fluorousphosphine)_3$ as the catalyst was reviewed. More than 53 references [107].

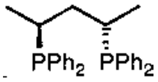
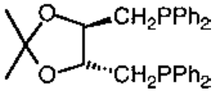
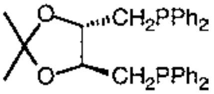
6. Advances in aqueous biphasic catalysis by water-soluble phosphine transition-metal complexes. A review with 147 references [108].
7. Reaction of olefins. Lower olefins. A review with 25 references about the basics of aqueous two-phase hydroformylation of C_3 and C_4 olefin with focus on TPPTS as a ligand and rhodium as the active metal center [109].
8. Kinetics of biphasic catalysis. A review with 25 references about the current status of the kinetics of hydroformylation of olefins using water-soluble catalysis. Kinetic studies for various reaction systems and the role of ligands, pH, co-solvents, and surfactants are reviewed [110].
9. The amphiphilic approach in aqueous-phase organometallic catalysis. A review with 30 references about rhodium catalysts with amphiphilic diphosphine ligands in olefin hydroformylation [111].
10. Organometallic molecular catalysts, small molecule machines. A review with 27 references on the topics of hydroformylation, asymmetric catalysis, and metallocene polymerization catalysts [112].
11. Hydroformylation of polyunsaturated fatty substances using homogeneous rhodium carbonyl/tertiary phosphine catalyst systems. A review with ca. 13 references [113].
12. Studies on the regioselectivity of the rhodium-catalyzed hydroformylation with alkenylalkoxysilanes. A review with six references [114].
13. Enantioselective hydroformylation of olefins catalyzed by rhodium(I) complexes of chiral phosphine-phosphite ligands. A review with 26 references [115].
14. Asymmetric hydroformylation by monometallic and bimetallic rhodium complexes. A review with 24 references [116].
15. Bimetallic homogeneous hydroformylation. A review with more than 44 references [117].
16. Catalysis of rhodium, rhodium-cobalt, and iridium-cobalt multinuclear complexes and its applications to organic syntheses. A review with 74 references on the preparation, reactions, and catalytic activity of the title cluster among others in silylformylation [118].
17. Some chiral ligands prepared for catalytic asymmetric reactions. A review with six references among others on synthesis and structure, and applications in D-mannitol or D-glucose based chiral bisphosphine catalytic hydroformylation [119].
18. From 2H-phospholes to BIPNOR, a new efficient bisphosphine for asymmetric catalysis. A review with 17 references describes the application of the new bisphosphine 2,2′-bis-(1-phosphanorbornadienyl) (BIPNOR) as a ligand on-rhodium(I) for asymmetric hydrogenation and hydroformylation of alkenes [120].
19. Development of transition metal phosphine complexes such as $[Pd(triphosphine)(solvent)](BF_4)_2$ (triphosphine = bis(2-dicyclohexyl-phosphinoethyl)phenylphosphine). A review, with 34 references including much of the author's work [121].
20. Photocatalyst for carbon dioxide reduction. A review with six references [122].

21. Recent developments of hydroformylation of olefins of higher molecular weight into oxo-alcohols. A review with 55 references about the scope and limits of applications for heteroge nized hydroformylation catalyst systems, micellar two-phase hydroformylation using surfactant phosphine ligands, and the hydroformylation with non-ionic surfactant phosphine catalyst systems [123].
22. Hydroformylation. Development of commercial biphasic oxo synthesis. A review with references [124].

Acknowledgements

The author thanks the Hungarian Science Fund for support under Grant No. OTKA 25028 and the Hungarian Ministry of Culture and Education for support under Grant No. 0801/1997.

Appendix A. Nomenclature

Ac	acetyl
acac	acetylacetonate
BCOS	**37**
(+)-BDPP	(+)-(2*R*,4*R*)-bis(diphenylphosphino)pentane
	
BINAPHOS	see **16**
Bn	benzyl
bpy	2,2′-bipyridine
Bz	benzoyl
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
Hdmg	monoanion of dimethylglyoxime
^{c}Hex	cyclohexyl
^{n}Hex	*n*-hexyl
IR	infrared
Ms	methanesulfonyl
MV^{2+}	methyl viologen, 1,1′-4,4′-bipyridinium
NBD	norbornadiene
OTf	trifluoromethanesulfonate
Piv	pivaloyl
py	pyridine
pz	pyrazolate
r.t.	room temperature
TFA	trifluoroacetyl
THF	tetrahydrofuran
TPPMS	sodium-*m*-(diphenylphosphino)benzene sulfonate
TPPTS	trisodium salt of the trisulfonated triphenylphosphine
Tos	*p*-toluenesulfonyl

Appendix B. The metals and their associated references

Metal	Refs.
Zr	[93]
Mn	[68]
Re	[85]
Fe	[39,93]
Ru	[46,83,87,88,93–97]
Co	[1,40–42,63,67,82,98,118]
Rh	[2–34,37,38,42–45,47,62,64,65,67,69,75–81,89,90,99,102,104,107–111,113–118,120]
Ir	[35,86,118]
Ni	[71,100,101]
Pd	[25,70–74,84,121]
Pt	[25,36–39,66,91]
Cu	[92]
Zn	[22]
Sn	[66]

References

[1] G. Margheri, L. Rosi, A. Salvini, M. Bianchi, P. Frediani, J. Mol. Catal. A Chem. 132 (1998) 189.
[2] R. Shirt, M. Garland, D.W.T. Rippin, Anal. Chim. Acta 374 (1998) 67; CA 129 (1998) 250777.
[3] T. Takahashi, S. Ebata, H. Yamada, Synlett (1998) 381; CA 128 (1998) 270790.
[4] A. Orejón, C. Claver, L.A. Oro, A. Elduque, M.T. Pinillas, J. Mol. Catal. A Chem. 136 (1998) 279.
[5] S.T. Sarraf and J.L. Leighton, Tetrahedron Lett. 39 (1998) 6423; CA 129 (1998) 259987.
[6] B. Kitsos-Rzychon, P. Eilbracht, Tetrahedron 54 (1998) 10721; CA 129 (1998) 260312.
[7] T. Takahashi, K. Machida, Y. Kido, K. Nagashima, S. Ebata, T. Doi, Chem. Lett. (1997) 1291; CA 128 (1998) 61374.
[8] C. Bianchini, P. Frediani, A. Meli, M. Peruzzini, F. Vizza, Chem. Ber. Recl. 130 (1997) 1633.
[9] D. Kadyrov, J. Heinicke, M.K. Kindermann, D. Heller, C. Fischer, R. Selke, A.K. Fischer, P.G. Jones, Chem. Ber. Recl. 130 (1997) 1663.
[10] T. Takahashi, S. Ebata, T. Doi, Tetrahedron Lett. 39 (1998) 1369; CA 128 (1998) 230178.
[11] A. Caiazzo, R. Settambola, G. Uccello-Barretta, R. Lazzaroni, J. Organomet. Chem. 548 (1997) 279.
[12] R. Settambola, A. Caiazzo, R. Lazzaroni, Synth. Commun. 27 (1997) 4111; CA 128 (1998) 61387.
[13] R. Settambola, S. Scamuzzi, A. Caiazzo, R. Lazzaroni, Organometallics 17 (1998) 2127.
[14] B. Breit, S.K. Zahn, Tetrahedron Lett. 39 (1998) 1901; CA 128 (1998) 282726.
[15] B. Breit, Eur. J. Org. Chem. (1998) 1123.
[16] D. Gleich, R. Schmid, W.A. Herrmann, Organometallics 17 (1998) 2141.
[17] X. Xu, H. Zhou, J. Chen, H. Fu, Fenzi Cuihua, 11 (1997) 374; CA 128 (1998) 4864.
[18] A. Orejón, A.M. Masdeu-Bultó, R. Echarri, M. Diéguez, J. Forniés-Cámer, C. Claver, C.J. Cardin, J. Organomet. Chem. 559 (1998) 23.
[19] N. Ruiz, A. Aaliti, J. Forniés-Cámer, A. Ruiz, C. Claver, C.J. Cardin, D. Fabbri, S. Gladiali, J. Organomet. Chem. 545–546 (1997) 79.
[20] S. Sirol and P. Kalck, New J. Chem. 21 (1997) 1129; CA 128 (1998) 23018.
[21] I. Bach and D.J. Cole-Hamilton, Chem. Commun. (1998) 1463.
[22] M. Moszner, A.M. Trzeciak, J.J. Ziolkowski, J. Mol. Catal. A Chem. 130 (1998) 241.
[23] W. Chen, Y. Xu, S. Liao, J. Mol. Catal. A Chem. 129 (1998) 153.
[24] E.A. Karakhanov, Yu. S. Kardasheva, E.A. Runova, V.A. Semernina, Neftekhimiya 38 (1998) 32; CA 129 (1998) 81503.
[25] Z. Csók, G. Szalontai, G. Czira, L. Kollár, J. Organomet. Chem. 570 (1998) 23.
[26] S.-H. Kyung, Han'guk Nanghwa Hakhoechi 40 (1997) 588; CA 128 (1998) 154205.
[27] W. Chen, Y. Xu, S. Liao, Acta Chem. Scand. 52 (1998) 285; CA 128 (1998) 229988.
[28] E. Fernández, A. Ruiz, C. Claver, S. Castillón, A. Pola, J.F. Piniella, A. Alvarez-Larena, Organometallics 17 (1998) 2857.
[29] E.M. Campi, J.W. Roy, A.E. Trnacek, Aust. J. Chem. 50 (1997) 1031; CA 128 (1998) 102064.
[30] E.M. Campi, W.R. Jackson, A.E. Trnacek, Aust. J. Chem. 50 (1997) 807; CA 128 (1998) 22679.
[31] H. Bahrmann, M. Haubs, T. Müller, N. Schopper, B. Cornils, J. Organomet. Chem. 545–546 (1997) 139.
[32] N. Karodia, S. Guise, C. Newlands, J.-A. Andersen, Chem. Commun. (1998) 2341.
[33] Y. Ohgomori, N. Suzuki, N. Sumitani, J. Mol. Catal. A Chem. 133 (1998) 289.
[34] Y. Jiang, S. Xue, Z. Li, J. Deng, A. Mi, A.S.C. Chan, Tetrahedron Asym. 9 (1998) 3185.
[35] G. Francio, R. Scopelliti, C.G. Arena, G. Bruno, D. Drommi, F. Faraone, Organometallics 17 (1998) 338.
[36] P. Meessen, D. Vogt, W. Keim, J. Organomet. Chem. 551 (1998) 165.
[37] R. Kadyrov, D. Heller, R. Selke, Tetrahedron Asym. 9 (1998) 329.
[38] S. Cserépi-Szücs, I. Tóth, L. Párkányi, J. Bakos, Tetrahedron Asym. 9 (1998) 3135.
[39] B. Jedlicka, W. Weissensteiner, T. Kégl, L. Kollár, J. Organomet. Chem. 563 (1998) 37.
[40] T.A. Kainulainen, M.K. Niemela, A.O.I. Krause, Catal. Lett. 53 (1998) 97; CA 129 (1998) 190722.
[41] M. Rattay, D. Fenske, P. Jutzi, Organometallics 17 (1998) 2930.

[42] L. Huang, Y. Xu, Catal. Lett. 53 (1998) 177; CA 129 (1998) 180611.
[43] K. Nozaki, Y. Itoi, F. Shibahara, E. Shirakawa, T. Ohta, H. Takaya, T. Hiyama, J. Am. Chem. Soc. 120 (1998) 4051.
[44] H. Gao, R.J. Angelici, Organometallics 17 (1998) 3063.
[45] Y. Zhang, Y. Yuan, Z. Chen, G. Lin, H. Zhang, Xiamen Daxue Xuebao, Ziran Kexueban 37 (1998) 228; CA 129 (1998) 135801.
[46] J.-X. Gao, P.-P. Xu, R.-H. Zheng, P.-Q. Huang, H.-L. Wan, K.-R. Tsai, J. Nat. Gas Chem. 6 (1997) 284; CA 128 (1998) 24235.
[47] R.M. Deshpande, B.M. Bhanage, S.S. Divekar, S. Kanagasabapathy, R.V. Chaudhari, Ind. Eng. Chem. Res. 37 (1998) 2391; CA 128 (1998) 294486.
[48] G. Fremy, E. Monflier, J.-F. Carpentier, Y. Castanet, A. Mortreux, J. Mol. Catal A Chem. 129 (1998) 35.
[49] V.S. Nair, B.M. Bhanage, R.M. Deshpande, R.V. Chaudhari, Stud. Surf. Sci. Catal. 113 (1998) 529; CA 129 (1998) 95186; Mol. Catal. A Chem. 129 (1998) 35.
[50] M. Schreuder Goedheijt, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Mol. Catal. A Chem. 134 (1998) 243.
[51] F.P. Pruchnik, P. Smolenski, K. Wajda-Hermanowicz, J. Organomet. Chem. 570 (1998) 63.
[52] R. Chen, X. Liu, Z. Jin, J. Organomet. Chem. 571 (1998) 201.
[53] P. Stoessel, H.A. Mayer, F. Auer, Eur. J. Inorg. Chem. (1998) 37; CA 128 (1998) 135756.
[54] X.-L. Zheng, R.-F. Chen, Z.-L. Jin, Gaodeng Xuexiao Huaxue Xuebao 19 (1998) 574; CA 128 (1998) 275628.
[55] E. Mieczynska, A.M. Trzeciak, R. Grzybek, J.J. Ziolkowski, J. Mol. Catal. A Chem. 132 (1998) 203.
[56] S.U. Son, J.W. Han, Y.K. Chung, J. Mol. Catal. A Chem. 135 (1998) 35.
[57] A.N. Ajjou, H. Alper, J. Am. Chem. Soc. 120 (1998) 1466.
[58] P. Kalck, L. Miquel, M. Dessoudeix, Catal. Today 42 (1998) 431; CA 129 (1998) 260036.
[59] B. Fell, P. Hermanns, H. Bahrmann, J. Pract. Chem. Chem. Ztg. 340 (1998) 459.
[60] E. Fernandez, A. Polo, A. Ruiz, C. Claver, S. Castillon, Chem. Commun. (1998) 1803; CA 129 (1998) 290286.
[61] O. Wachsen, K. Himmler, B. Cornils, Catal. Today 42 (1998) 373; CA 129 (1998) 291371.
[62] I.T. Horváth, G. Kiss, R.A. Cook, J.E. Bond, P.A. Stevens, J. Rábai, E. Mozeleski, J. Am. Chem. Soc. 120 (1998) 3133.
[63] R. Tannenbaum, U.K. Dietler, G. Bor, F. Ungváry, J. Organomet.Chem. 570 (1998) 39.
[64] G.J.H. Buisman, L.A. van der Veen, P.C.J. Kamer, P.W.N.M. van Leeuwen, Organometallics 16 (1997) 5681.
[65] A. Castellanos-Páez, S. Castillón, C. Claver, P.W.N.M. van Leeuwen, W.G.J. de Longe, Organometallics 17 (1998) 2543.
[66] T. Kégl, L. Kollár, L. Radics, Inorg. Chim. Acta 265 (1997) 249.
[67] I. Ojima, Z. Li, R.J. Donovan, P. Ingallina, Inorg. Chim. Acta 270 (1998) 279.
[68] S.B. Halligudi, D. Chatterjee, D.B. Shukla, R.S. Somani, Stud. Surf. Sci. Catal. 113 (1998) 841; CA 129 (1998) 55698.
[69] P. Serp, L. Chateau, R. Feurer, A. Kiennemann, P. Kalck, J. Mol. Catal. A Chem. 136 (1998) 269.
[70] M. Schreuder Goedheijt, J.N.H. Reek, P.S.J. Kamer, P.W.N.M. van Leeuwen, Chem. Commun. (1998) 2431.
[71] B.-S. Wan, S.-J. Liao, Y. Xu, D.-R. Yu, J. Mol. Catal. A Chem. 136 (1998) 263.
[72] H. Zhou, J. Hou, J. Chen, S. Lu, H. Fu, H. Wang, Cuihua Xuebao 19 (1998) 247; CA 129 (1998) 54131.
[73] M. Beller, M. Eckert, F. Vollmüller, J. Mol. Catal. A Chem. 135 (1998) 23.
[74] W.-J. Xiao, G. Vasapollo, H. Alper, J. Org. Chem. 63 (1998) 2609.
[75] B. Breit, Tetrahedron Lett. 39 (1998) 5163.
[76] D.J. Bergmann, E.M. Campi, J.W. Roy, Q.J. Mccubbin, A.F. Patti, Tetrahedron 53 (1997) 17449; CA 128 (1998) 102067.
[77] T. Rische, P. Eilbracht, Tetrahedron 54 (1998) 8441; CA 129 (1998) 189071.
[78] T. Rische, P. Eilbracht, Synthesis (1997) 1331.

[79] C.L. Kranemann, P. Eilbracht, Synthesis (1998) 71.
[80] T. Rische, B. Kitsos-Rzychon, P. Eilbracht, Tetrahedron 54 (1998) 2723; CA 128 (1998) 230085.
[81] L. Bärfacker, C. Hollmann, P. Eilbracht, Tetrahedron 54 (1998) 4493.
[82] M.L.N. Rao, M. Periasamy, J. Organomet. Chem. 553 (1998) 91.
[83] T. Fukuyama, N. Chatani, J. Tatsumi, F. Kakiuchi, S. Murai, J. Am. Chem. Soc. 120 (1998) 11522.
[84] J. Scheele, P. Timmermann, D.N. Reinhoudt, Chem. Commun. (1998) 2613.
[85] M. Fernandez, M. Mediavilla, P. Baricelli, S.A. Moya, A.J. Pardey, Ciencia (Maracaibo) 6 (1998) 112; CA 129 (1998) 281694.
[86] M. Fernandez, M. Meza, M. Mediavilla, C. Longo, S.A. Moya, F. Lopez, P. Baricelli, A.J. Pardey, An. Quim. Int. Ed. 94 (1998) 127; CA 129 (1998) 266128.
[87] O.K. Kallinen, T.T. Pakkanen, T.A. Pakkanen, J. Organomet. Chem. 547 (1998) 93621.
[88] M. Haukka, T. Venäläinen, M. Kallinen, T.A. Pakkanen, J. Mol. Catal. A Chem. 136 (1998) 127.
[89] M.M. Mdleleni, R.G. Rinker, P.C. Ford, Inorg. Chim. Acta 270 (1998) 345.
[90] C. Linares, M. Mediavilla, A.J. Pardey, P. Baricelli, C. Longo-Pardey, S.A. Moya, Catal. Lett. 50 (1998) 183; CA 128 (1998) 235643.
[91] M. Ichikawa, T. Yamamoto, W. Pan, T. Shido, Stud. Surf. Sci. Catal. 105A (1997) 679; CA 128 (1998) 209399.
[92] M. Mediavilla, D. Pineda, F. Lopez, D. Moronta, C. Longo, S.A. Moya, P.J. Baricelli, A.J. Pardey, Polyhedron 17 (1998) 1621; CA 129 (1998) 20087.
[93] Y. Chen, H. Xu, W. Xu, Zhejiang Nangye Daxue Xuebao 24 (1998) 255; CA 129 (1998) 180608.
[94] H.S. Chu, C.P. Lau, K.Y. Wong, W.T. Wong, Organometallics 17 (1998) 2768.
[95] P. Frediani, C. Foggi, A. Salvini, M. Bianchi, F. Piacenti, Inorg. Chim. Acta 272 (1998) 141.
[96] M.M. Ali, H. Sato, T. Mizukawa, K. Tsuge, M. Haga, K. Tanaka, Chem. Commun. (1998) 249.
[97] R. Ziessel, L. Toupet, S. Chardon-Noblat, A. Deronzier, D. Matt, J. Chem. Soc. Dalton Trans. (1997) 3777; CA 128 (1998) 9752.
[98] D. Behar, T. Dhanasekaran, P. Neta, C. M. Hosten, D. Ejeh, P. Hambright, E. Fujita, J. Phys. Chem. A. 120 (1998) 2870; CA 128 (1998) 286833.
[99] C.S. Pomelli, J. Tomasi, M. Solá, Organometallics 17 (1998) 3164.
[100] R.E. Wittrig, G.M. Ferrence, J. Washington, C.P. Kubiak, Inorg. Chim. Acta 270 (1998) 111.
[101] I. Tommasi, M. Aresta, P. Giannoccaro, E. Quaranta, C. Fragale, Inorg. Chim. Acta 272 (1998) 38.
[102] Y. Musashi, S. Sakaki, J. Chem. Soc. Dalton Trans. (1998) 577.
[103] A. Muramatsu, Kinzoku, 68 (1998) 323; CA 128 (1998) 257159.
[104] D. Chen, Y. Yuan, Q. Cai, Tianranqi Huagong 22 (1997) 41; CA 128 (1998) 36301.
[105] B. Cornils, Org. Process Res. Dev. 2 (1998) 121; CA 128 (1998) 142269.
[106] X. Zheng, X. Liu, Z. Jing, Tianranqi Huagong 22 (1997) 36; CA 128 (1998) 22611.
[107] I.T. Horváth, Acc. Chem. Res. 31 (1998) 641.
[108] H. Chen, Y. Li, D. Li, P. Cheng, X. Li, Huaxue Jinzhan 10 (1998) 146; CA 129 (1998) 175659.
[109] C.D. Frohning, C.W. Kohlpaintner, Aqueous-Phase Organomet. Catal. (1998) 294; CA 129 (1998) 221702.
[110] R.V. Chaudhari, B.M. Bhanage, Aqueous-Phase Organomet. Catal. (1998) 283; CA 129 (1998) 221701.
[111] P.C.J. Kamer, P.W.N.M. Van Leeuwen, Aqueous-Phase Organomet. Catal. (1998) 564; CA 129 (1998) 221703.
[112] C. Lensik, N. B. Milestone, Chem. N. Z. 61 (1997) 20.
[113] B. Fell, Oils-Fats-Lipids 1995, Proc. World Congr. Int. Soc. Fat Res., 21st 3 (1995) 461 (Publ. 1996); CA 128 (1998) 129407.
[114] M. Wessels, J. Grobe, Organosilicon Chem. III, [München, Silicontage, 1996] Publ. 1998. 538; CA 128 (1998) 230428.
[115] K. Nozaki, H. Takaya, T. Hiyama, Top. Catal. 4 (1998) 175; CA 128 (1998) 229901.
[116] G.G. Stanley, Adv. Catal. Processes 2 (1997) 221; CA 128 (1998) 257003.
[117] G.G. Stanley, Catal. Di- Polynucl. Met. Cluster Complexes (1998) 345; CA 128 (1998) 244074.

[118] I. Ojima, Z. Li, Catal. Di-Polynucl. Met. Cluster Complexes (1998) 307; CA 128 (1998) 244073.
[119] S. Lu, L. Wang, Fenzi Cuihua 11 (1997) 476; CA 128 (1998) 206132.
[120] F. Mathey, F. Mercier, F. Robin, L. Ricard, J. Organomet. Chem. 557 (1998) 117.
[121] D.L. Dubois, Comments Inorg. Chem. 19 (1997) 307; CA 128 (1998) 209977.
[122] O. Ishitani, Zosui Gijutsu 24 (1998) 40; CA 129 (1998) 295977.
[123] B. Fell, Tenside, Surfactants, Deterg. 35 (1998) 326; CA 129 (1998) 303998.
[124] B. Cornils, E. G. Kuntz, Aqueous-Phase Organomet. Catal. (1998) 271; CA 129 (1998) 317862.