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Application of transition metals in hydroformylation. Annual survey covering the year 1995

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Abstract

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

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

List of abbreviations

acac	acetylacetonate
bpy	2,2′-bipyridine

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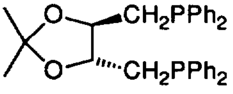
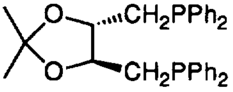
^{c}Hx	cyclohexyl
^{c}Pe	cyclopentyl
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
(−)-DIOP	(2*R*,3*R*)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane 
(+)-DIOP	(2*S*,3*S*)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane 
DMF	*N*,*N*-dimethylformamide
DMSO	dimethylsulfoxide
dppb	$Ph_2PCH_2CH_2CH_2CH_2PPh_2$
dppe	$Ph_2PCH_2CH_2PPh_2$
dppp	$Ph_2PCH_2CH_2CH_2PPh_2$
dppoo	$Ph_2PCH_2CH_2OCH_2CH_2OCH_2CH_2PPh_2$
ee	enantiomeric excess
1,5-hd	1,5-hexadiene
phen	1,10-phenanthroline
py	pyridine
r.t.	room temperature
THF	tetrahydrofuran
TPPTS	trisodium salt of trisulfonated triphenylphosphine

1. Hydroformylation

1.1. Homogeneous systems

1.1.1. Cobalt catalysts

The catalytic activity in ethylene hydroformylation of octacarbonyl dicobalt on zinc oxide was correlated with the formation of homonuclear ion-pairing surface species, $Co^{2+}/Co(CO)_4^-$ [1]. The hydroformylation of butenes and butane–butene distillation fractions by syngas was studied using $Co_2(CO)_8$ as the catalyst precursor. The effect of the reaction conditions on the reaction rate and selectivity of C_5 aldehyde and alcohol formation was studied. Activation and pre-exponent values of hydroformylation were calculated for the 120–180 °C temperature range [2]. The C_5 fractions obtained from ethylene plants were used in the production of fatty alcohols by hydroformylation in the presence of cobalt catalysts. At 180 °C and 60–70 bar $H_2/CO = 2.5/1$, a 75% yield of fatty alcohols was obtained [3].

The effect of solvent polarity on the isomeric ratio of the products was studied in the octacarbonyldicobalt-catalyzed hydroformylation at 100 bar synthesis gas pressure ($CO/H_2 = 1/1$) at 100 °C. Whereas non-polar solvents, such as heptane or cyclohexane, do not affect the ratio of *n*- to iso-products formed from 1-hexene, polar solvents, such as DMF, methanol or acetonitrile, favor an increased formation of the iso-products. The extent of iso-products increases with increasing solvent Lewis basicity. The effect has been discussed in relation to the stabilization of intermediate cationic complexes [4].

The formation of dimers in the octacarbonyl dicobalt- and $RhCl(PPh_3)_3$-catalyzed hydroformylation of 1-hexene and styrene was studied in pyridine as solvent [5].

The catalysis of cobalt-tetra(diphenylphosphino)neopentane systems for the hydroformylation of acrylic acid esters has been investigated. The effects of reaction temperature, pressure, molar ratios of phosphorus to cobalt and various olefins were studied. The comparison of other catalyst systems prepared from cobalt-diphosphines with these new catalyst systems for the hydroformylation of acrylic acid esters shows that their catalytic activities have the following order: $C(CH_2PPh_2)_4 > Ph_2P(CH_2)_2PPh_2 > Ph_2P(CH_2)_3PPh_2 > Ph_2PCH_2PPh_2 \approx Ph_2P(CH_2)_4PPh_2$ [6] (see also Ref. [7]).

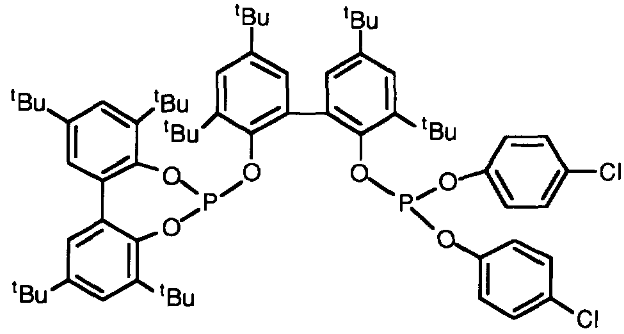
1.1.2. *Rhodium catalysts*

The influence of temperature on the regioselectivity in the rhodium-catalyzed hydroformylation of ethyl vinyl ether and ethyl allyl ether was investigated in the temperature range 20–120 °C. For both substrates, the amount of branched aldehyde decreases as the temperature increases. The ^2H nuclear magnetic resonance (NMR) investigation of the deuterioformylation products obtained at partial conversion revealed the different behavior of the metal alkyl intermediates: at room temperature, their formation is irreversible; at high temperature, it becomes reversible for both isomers in the case of ethyl vinyl ether, but only for the branched isomer in the case of ethyl allyl ether [8].

The deuterioformylation of 1-hexene, catalyzed by (chelating diphosphine)-rhodium catalysts, gave nearly exclusively $CH_3(CH_2)_3CHDCH_2CDO$ and $CH_3(CH_2)_3CH(CH_2D)CDO$, with the deuterium labels at the β-carbon and at the aldehyde carbon. Very little deuterium was incorporated into the recovered hexenes. These results establish that the regiochemistry of aldehyde formation is set by a largely irreversible addition of rhodium hydride to complexed 1-hexene to produce an alkylrhodium intermediate which is committed to aldehyde formation [9].

The rhodium-catalyzed hydroformylation of 1-octene, cyclohexene, and styrene has been studied using $Rh(CO)_2(acac)$ as the catalyst precursor and tris(2-tert-butyl-4-methylphenyl)phosphite as the ligand at 40–100 °C, $P_{CO} = 2.5$–44 bar and $P_{H2} = 2.5$–50 bar in toluene as solvent. For 1-octene, very high hydroformylation rates are obtained (39.8×10^3 mol (mol Rh)$^{-1}$ h^{-1}) under mild conditions ($P_{CO} = 10$ bar, $P_{H2} = 10$ bar, 80 °C). The concentration dependences of the reaction rate show that the rate-determining step is the reaction of H_2 with the acylrhodium complex. A negative order in the CO concentration is observed. For cyclohexene, the reaction rate is lower under the same conditions, and the addition of cyclohexene to the starting rhodium hydride complex is rate limiting. In the hydroformylation of styrene, the rate is three times lower than that of 1-octene. For the formation of the linear 3-phenylpropanal, the rate-determining step is the reaction of H_2 with the acylrhodium species. CO inhibits the reaction. In contrast with the formation of the secondary 2-octyl species from 1-octene, the formation of the secondary (1-phenylethyl)rhodium species is reversible [10].

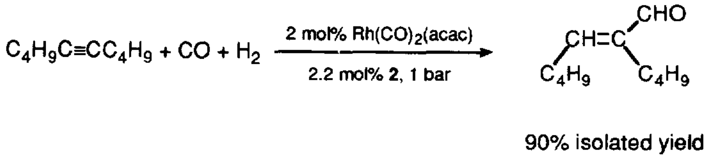
The crystal structure and characterization in solution of $RhH(CO)_2$ (**1**) have been described. The complex is a highly regioselective hydroformylation catalyst for 1-octene at 60 °C and 20 bar $CO/H_2 = 1/1$, leading to a normal to branched aldehyde ratio of 15 [11].

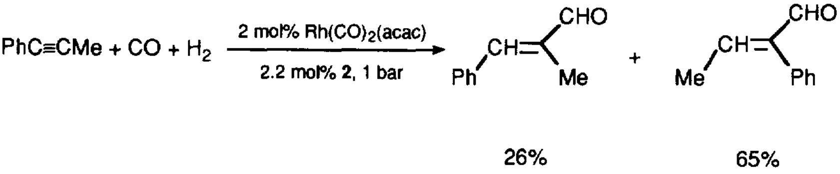


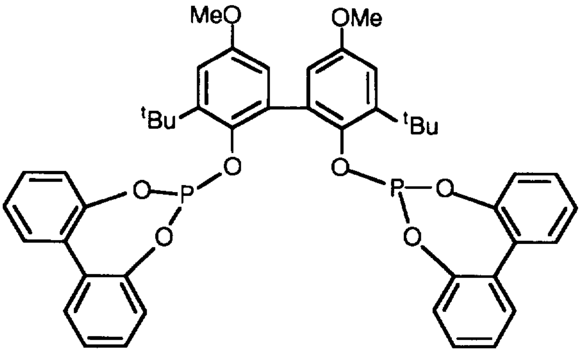
1

The rhodium-catalyzed hydroformylation of 1-octene using the bis(phosphite) ligand **2** was studied by in situ, high-pressure ^1H and ^{31}P NMR and Fourier transform infrared (FTIR) spectroscopy. Four species, Rh(**2**)(acac), $Rh(\mathbf{2})(CO)_2H$ and two dimeric complexes appeared sequentially during different stages of the catalysis when $Rh(acac)(CO)_2$ was used as the catalyst precursor. These were independently synthesized and their reactivity studied. The major species present during catalysis is $Rh(\mathbf{2})(CO)_2H$, which was fully characterized [12].

Disubstituted alkynes were selectively hydroformylated at room temperature and 1 bar pressure ($CO/H_2 = 1$) in methylene chloride as solvent using $Rh(CO)_2(acac)$ and **2** as the catalyst precursor [13], e.g.

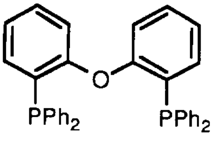






2

The effect of the bite angle on the regioselectivity in the rhodium-catalyzed hydroformylation reaction was studied with bidentate diphosphines **3**–**7** based on xanthene-like backbones as ligands. The bite angles of these ligands are fine tuned by subtle alterations of the backbone of the ligands. In the hydroformylation of 1-octene, the regioselectivity increased regularly with increasing bite angle. At 40 °C, up to 98.3% *n*-aldehyde was obtained with **6**, without isomerization or hydrogenation of 1-octene. The ligand **6** induces the highest selectivity so far reported for the formation of the linear aldehyde for diphosphines in the hydroformylation of 1-alkenes [14].



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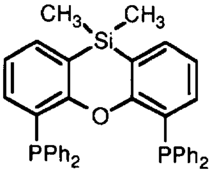

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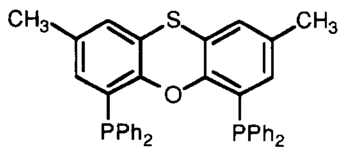

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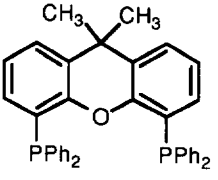

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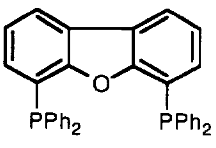


7

The mechanism of the low-pressure hydroformylation of allyl alcohol, in the presence of $RhH(CO)(PPh_3)_3$ as catalyst, was studied using FTIR and NMR techniques [15]. The effects of phosphorus-containing promoters and solvents on the selectivity of the (acetylacetonato)dicarbonylrhodium-catalyzed hydroformylation of dihydromyrcenol was studied. The product compositions were analyzed by in situ IR spectroscopy. The rhodium-containing intermediates were discussed [16]. A cationic rhodium complex with a cavity-shaped phosphine ligand was found to catalyze the hydroformylation of styrene at 40 °C, under a CO/H_2 pressure of 40 bar, leading to 2-phenylpropanal and 3-phenylpropanal in the ratio 95 : 5 [17]. The hydroformylation of styrene and *p*-methylstyrene catalyzed by $Rh(acac)(CO)_2$ was studied under atmospheric pressure. Complexes containing phosphine ligands showed higher catalytic activity than $Rh(acac)(CO)_2$ alone in the order $Ph_3P < Ph_2P(CH_3)_3PPh_2 < Ph_2P(CH_3)_2PPh_2 < P(OPh)_3$. Up to 95% of 2-arylpropanal can be obtained in the presence of diphosphine ligands [18]. Three dirhodium(II) complexes, including orthometallated triphenylphosphine ligands, have been tested as catalytic precursors for the hydroformylation of styrene. The activities obtained and the wide range of selectivities have been compared with the same reaction performed with $RhH(CO)(PPh_3)_3$, $Rh_2(O_2CCH_3)_4$ and various amounts of triphenylphosphine [19]. The influence of various parameters on the hydroformylation of olefins, using $Rh_2(O_2CCH_3)_4/PBu_3/EtOH$ and $Rh_6(CO)_{16}/PBu_3/EtOH$ catalytic systems, was studied. The hydroformylation of 1-heptene was found to be rapid. The olefin was converted in 95% yield to octanals in 2 h. However, the hydrogenation to the corresponding alcohol was very slow, taking at least 22 h at 100–120 °C to obtain a conversion of 100% [20].

Hydrocarbonylations of alkenamides and novel silylcarbocyclization reactions catalyzed by rhodium and rhodium/cobalt complexes were studied [7]. The $[\{Rh(CO)_2Cl\}_2]/PPhMe_2$-catalyzed hydroformylation of 2-vinylpyridine was found to give the branched aldehyde 2-(2-pyridyl)propanal in good yield and 99% α-regioselectivity [21].

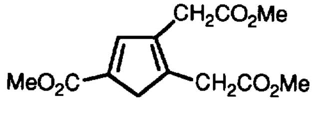
Polybutadiene polyols were synthesized by a two-step process of controlled hydroformylation, followed by reduction of the formyl groups, to place a desired amount of pendant alcohol groups along the polymer chain. The degree of functionalization was controlled by measuring the gas uptake from a calibrated reservoir during hydroformylation. Hydroformylation was performed in solution or under simulated melt-phase conditions using either $RhH(CO)(PPh_3)_3$ or $Rh(acac)(CO)_2$ as catalysts. Reduction of the polyaldehyde by $NaBH_4$ generates the polymeric alcohol without reduction of the remaining double bonds [22].

A variety of amphiphilic ligands, Ph_2ArP ($Ar \equiv$ 3-hydroxyphenyl, 4-carboxyphenyl), Ph_nAr_{3-n} ($Ar \equiv 4\text{-}PhCH_2X$, $X \equiv NEt_2$, NMePh, NPh_2; $n = 1\text{–}2$) and $Ph_nAr_{3-n}P$ ($Ar \equiv$ 3/4-pyridyl; $n = 1\text{–}2$), in the rhodium-catalyzed hydroformylation of 1-octene (80 °C, 20 bar syngas, toluene) were found to be comparable with triphenylphosphine. In all cases, the aldehydes were formed with a normal to iso ratio of 2.8. The new ligands in their protonated, water-soluble form do not produce active hydroformylation catalysts [23].

The kinetics of hydroformylation of isobutene in the presence of $(acac)Rh(CO)_2$, modified with etriol phosphite, were investigated. The reaction was found to be first order in isobutene and the activation energy for Me_2CHCH_2CHO formation is 78 ± 2 kJ mol^{-1} [24].

The rhodium complexes obtained from $[\{RhCl(L)_2\}_2]$ ($L \equiv CO$, C_2H_4 or

1,5-cyclooctadiene) and **8** were found to be efficient catalysts for the hydroformylation of styrene and 1-hexene. Using this catalyst in the presence of PPh_3, high yields of the branched aldehydes were obtained [25].



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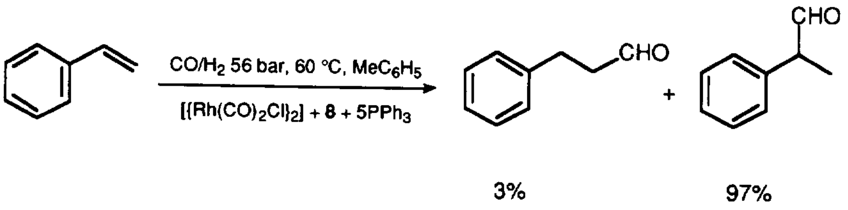
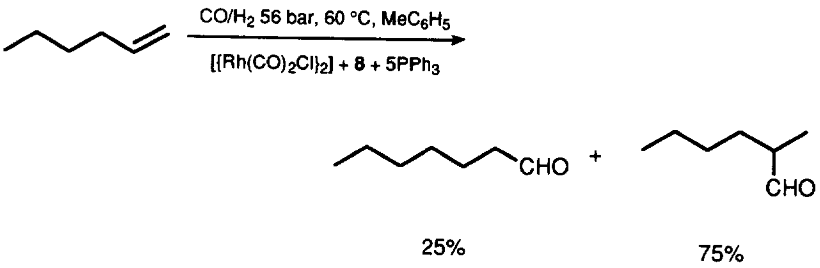
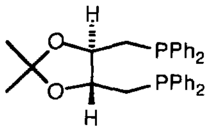




Acrolein acetals were hydroformylated by the rhodium-triarylphosphine system. Excellent rates and selectivity to succinaldehyde monoacetal were obtained using 4,4,6-trimethyl-2-vinyl-1,3-dioxane and tris(3,5-dichlorophenyl)phosphine as the acrolein acetal and phosphine ligand respectively. The key roles of the substituents of the phosphine and the acrolein acetal in the promotion of the reaction were also discussed [26].

1,4-Butanediol was obtained in approximately 79% overall yield by the hydroformylation of acrolein acetal in the presence of rhodium-diphosphine catalysts (prepared from acetylacetonatodicarbonylrhodium and diphosphines **9**–**11**), followed by subsequent hydrolysis/hydrogenation of the products over ruthenium and heteropolyacid catalysts supported on carbon. DIOP (**9**) was found to be a highly efficient ligand in the hydroformylation reaction producing the desired intermediate to 1,4-butanediol. Preliminary cost evaluation revealed that this method is promising for industrial application [27].

The hydroformylation of formaldehyde to glycolaldehyde in the presence of $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$ and $RhCl_3 + PPh_3$ precatalysts in *N*,*N*-dimethylacetamide was studied. The optimum conditions for formaldehyde hydroformylation were found to be: $RhCl_3 + PPh_3$ as the catalyst precursor, $T \leq 383$ K, $P \geq 120$ bar



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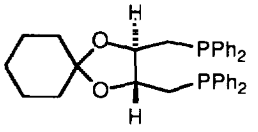

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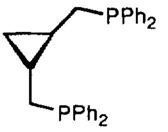

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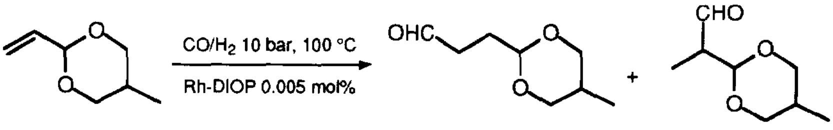
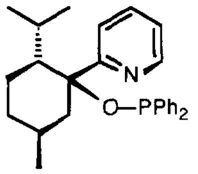


99.9% conversion, 99.1% aldehyde selectivity, 5.11 n/i ratio

pressure ($CO/H_2 = 1/1$), $[H_2O] \leq 1.8$ M, $[Rh] = 2.5 \times 10^{-3}$ g-atom Rh l^{-1}, paraformaldehyde concentration in the starting mixture, no more than 0.03 g l^{-1}. At a substrate conversion of 62%–67%, the selectivity of glycolaldehyde formation was found to be 96%, and the yield was 60%–65% [28].

Rhodium complexes with dithiolate bridges, such as $[Rh_2(\mu\text{-}S(CH_2)_nS)(COD)_2]$ ($n = 2$, 3 or 4; COD, 1,5-cyclooctadiene), were used as catalyst precursors for 1-hexene hydroformylation. The influence of different dithiolates and phosphines on the catalytic activity and selectivity was explored [29].

Cationic rhodium(I) complexes containing the new chiral bidentate P,N-ligand **12** were prepared and used successfully in the enantioselective hydroformylation of styrene, 2-vinylnaphthalene, methyl acrylate and vinyl acetate. The best results were achieved for 2-vinylnaphthalene and methyl acrylate [30].



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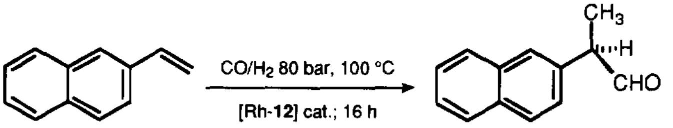
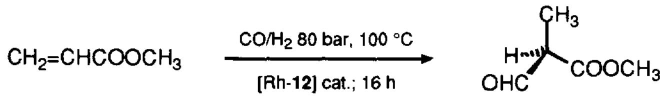
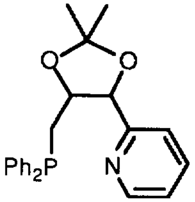


100% conversion
100% branched
78% ee (R)



95% conversion
97% branched
92% ee (R)

The catalytic hydroformylation of styrene, vinyl acetate and phenyl vinyl ether was studied using the chiral optically active pyridyl phosphine **13** and its phosphine-oxide **14** as ligands with rhodium complexes. In most cases, these hydroformylation reactions provide good chemoselectivity and regioselectivity, but unsatisfactory enantioselectivity. The rhodium(I) complex containing **14** was found to be remarkably more active than the catalyst formed with **13** [31].



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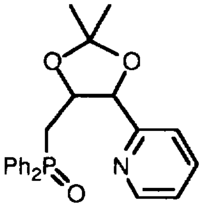

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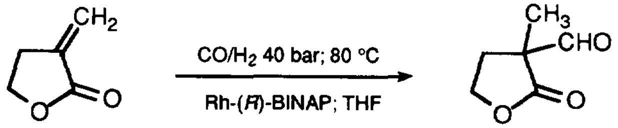
The asymmetric hydroformylation of styrene was performed using the bridged dithiolate chiral rhodium complexes $[Rh_2(\mu\text{-}(-)\text{-DIOS})(COD)_2]_n$ ($n = 1$ and 2; DIOS, 2,3-O-isopropylidene-1,4-dithio-L-threitol) as catalyst precursors. The catalytic systems provide high conversion in the corresponding aldehydes (100% at 30 bar and 65 °C) with a selectivity in 2-phenylpropanal of 64%. The addition of PPh_3 to the catalytic system increases the selectivity in 2-phenylpropanal to 91% under the same conditions. The enantiomeric excess (ee) of (*S*)-2-phenylpropanal was low (3%–5%) [32]. Asymmetric hydroformylation of styrene was performed using dinuclear thiolato bridged rhodium complexes with BDPP (BDPP, 2,4-bis(diphenylphosphino)-pentane) as the chiral auxiliary ligand at 65 °C and 30 bar ($CO/H_2 = 1/1$) in THF solution. In the best case at 80% conversion, the 2-phenylpropanal to 3-phenylpropanal ratio was 94 : 6 and 43% ee of the (*S*)-isomer was observed [33].

The rhodium-catalyzed asymmetric hydroformylation of styrene with chiral diphosphite ligands based on sugar backbones was studied. High regioselectivities (up to 97%) to the branched aldehyde were found at 25–40 °C and 9–45 bar of syngas pressure. Enantioselectivities up to 64% were obtained [34].

The effect of 1,4-bis(diphenylphosphino)butane (dppb) on the regioselectivity of the hydroformylation of α,β-unsaturated esters with synthesis gas, catalyzed by rhodium(I) complexes, was investigated. Excellent regioselectivity was obtained when dppb was added as a ligand for the reaction of methyl acrylate and α-methylene-γ-butyrolactone with synthesis gas. However, dppb inhibits the reaction when methyl methacrylate is used as the substrate. The asymmetric hydroformylation of α-methylene-γ-butyrolactone using $[Rh(1,5\text{-hd})(phen)]^+Cl^-$ as catalyst (1,5-hd, 1,5-hexadiene; phen, 1,10-phenanthroline) and (*R*)-BINAP as the chiral ligand (6 : 1 ratio of (*R*)-BINAP to Rh) gave an aldehydic lactone, containing a quaternary chiral center, in up to 37% ee [35].



Chiral diphosphites based on (2*R*,3*R*)-butane-2,3-diol, (2*R*,4*R*)-pentane-2,4-diol, (2*S*,5*S*)-hexane-2,5-diol, (1*S*,3*S*)-diphenylpropane-1,3-diol and *N*-benzyltartaramide as chiral bridges have been used in the rhodium-catalyzed asymmetric hydroformylation of styrene. Enantioselectivities up to 76% at 50% conversion were obtained with stable hydridorhodium diphosphite catalysts. High regioselectivities (greater than 95%) and high conversion (greater than 99%) to 2-phenylpropanal were found under relatively mild reaction conditions (25–40 °C, 9 bar of pressure ($CO/H_2 = 1/1$)) [36] (see also Refs. [5,37,38]).

1.1.3. Other metals as catalysts and bimetallic catalysts

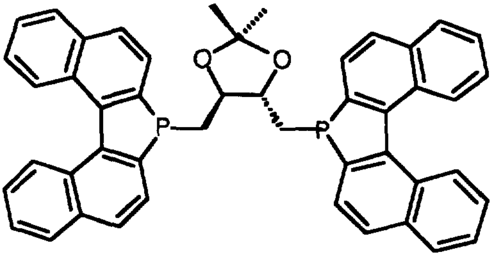
The selectivity for stoichiometric hydrogenation and hydroformylation of 3,3-dimethyl-1,2-diphenylcyclopropene with hydridopentacarbonylmanganese(I) was studied in supercritical CO_2, hexane and without solvent. Identical selectivities were found, suggesting that cage effects are either coincidentally identical or that aldehydes are primarily formed by non-radical pathways [39].

The hydroformylation of 1-heptene catalyzed by homogeneous and heterogeneous $Ru_3(CO)_{12}$ catalyst has been investigated. $Ru_3(CO)_{12}$ exhibits the maximum selectivity for aldehyde at 120 °C, and the normal to iso values of the aldehyde and alcohol decrease rapidly with increasing temperature [40]. Supported $Ru_3(CO)_{12}$ catalysts modified with $NaBH_4$ or KOH have higher activity and selectivity for aldehyde. The FTIR spectra of the catalysts after reaction show that $Ru_3(CO)_{12}$ is transformed to a hydrocarbonyl complex $[HRu_3(CO)_{11}]^-$, and $[NEt_4]Cl$ promotes the formation of $[HRu_3(CO)_{11}]^-$ and stabilizes it [41]. The ruthenium catalyst prepared from a triruthenium ketenylidene cluster was found to exhibit high catalytic activity in the hydroformylation of ethylene and CO hydrogenation compared with the catalyst from $[HRu_3(CO)_{11}]^-$. The high activity possibly resulted from the ketenyl group which may partly be converted to carbide species [42]. Ruthenium complexes of the type $[RuH(CO)(NCMe)(PR_3)(PPh_3)_2]BF_4$ (R ≡ Ph, OPh, ^{c}Hx) were found to be efficient, but not selective, catalysts for the hydroformylation of 1-hexene under moderate reaction conditions (120–150 °C, 100 bar $H_2/CO = 1/1$) [43]. Synthetic and real hydroformylation solutions containing 50–2000 $\mu g\ ml^{-1}$ ruthenium, 1-hexene, 1-heptanal and 1-heptanol were successfully analyzed by flame atomic absorption spectrometry after dilution with appropriate amounts of ethanol and toluene [44].

A chiral bimetallic hydroformylation catalyst system has been described which gives high enantioselectivities for a series of vinyl ester substrates. Molecular modeling studies have been presented to explain the high enantioselectivity [45]. Reactivity and mechanistic studies on bimetallic rhodium hydroformylation catalytic systems have been made [46].

The asymmetric hydroformylation of styrene catalyzed by platinum/tin complexes with chiral bis(binaphthophosphole) ligands **15**–**17** was studied. Under optimum conditions, reaction takes place with high (80%) branched selectivity and moderate enantioselectivity (up to 45% ee) to give predominantly (*S*)-2-phenylpropanal [47].

The hydroformylation of (+)-(*R*)-limonene, (+)-(1*R*)-isolimonene, camphene and (+)-β-cedrene resulted in the regiospecific formation of the corresponding linear aldehyde in the presence of homogeneous platinum and, in some cases, rhodium catalysts. The epimeric composition could be influenced slightly by optically active catalysts formed with chiral bidentate phosphines. The relative configurations of the newly formed sterogenic centers were analyzed by ^{1}H and ^{13}C NMR spectroscopy.



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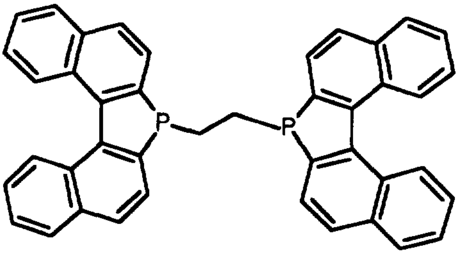

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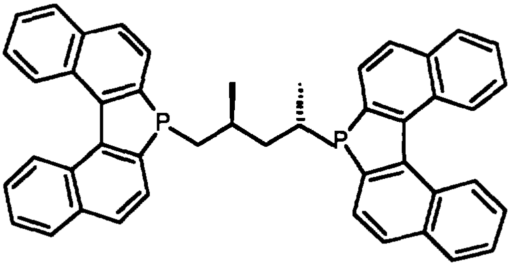
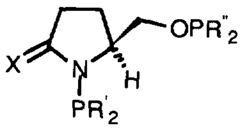


17

Despite the moderate diastereoselection, the products are of practical importance owing to their highly regioselective formation [37].

Platinum(II) aminophosphine- and amidophosphine-phosphinite complexes have been used in the catalytic asymmetric hydroformylation of styrene. The complexes $PtCl_2$(AMPP) (AMPP, **18**; derived from (*S*)-2-(hydroxymethyl)pyrrolidine and (*S*)-2-(hydroxymethyl)pyrrolidinone), in combination with $SnCl_2 \cdot 2H_2O$, were found to catalyze the asymmetric hydroformylation of styrene into (*S*)-2-phenylpropanal with 100 turnover in 15–200 h. The branched to normal ratios were 0.4–0.8 and the ee values varied between 40% and 56%. The best optical yields were observed with (dicyclohexylphosphino)oxy substituents [48].

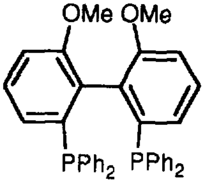


X = O, 2H

R', R'' = Ph, ^{c}Hx, ^{c}Pe

18

In the presence of $SnCl_2$, [$PtCl_2$(*S*)-(−)-**19**] was found to be an efficient catalyst for the asymmetric hydroformylation of styrene. The influence of CO and H_2 partial pressures on the catalytic activity was studied [49].



19

The reactions of the square planar methylplatinum-*cis*-diphosphine complexes, Pt(Me)(Cl){(*S*,*S*)-BDPP} and Pt(Me)($SnCl_3$){(*S*,*S*)-BDPP} (BDPP, (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane), with CO and a mixture of CO/H_2 have been studied in CD_2Cl_2 solutions by variable-temperature, high-pressure NMR spectroscopy to establish the role of the Pt–$SnCl_3$ bond in the CO insertion and hydrogenolysis steps of the Pt-diphosphine-catalyzed olefin hydroformylation reaction [50] (see also Ref. [7]).

1.2. Heterogeneous systems

1.2.1. Supported complexes

The catalytic activity of ruthenium 2,2′-bipyridine-derived catalysts in 1-hexene hydroformylation and 1-heptanal hydrogenation was studied. The $Ru_3(CO)_{12}$/2,2′-bipyridine/SiO_2 catalyst was found to be highly active in hydrogen transfer processes, such as the isomerization of alkenes and the hydrogenation of aldehydes to alcohols, as well as in the water–gas shift reaction and the hydroformylation of alkenes [51]. Ruthenium supported on rare earth oxides has been studied as a heterogeneous catalyst for 1-heptene hydroformylation under 50 bar $CO/H_2 = 1/1$ at 150°C for 20 h. CeO_2 was found to be the most efficient support. The FTIR spectra of the catalysts before and after the reaction indicate that ruthenium carbonyls are formed on the support surface during the hydroformylation and precarbonylation process [52].

The catalytic hydroformylation of 1-hexene by a polyalumazane/ruthenium/lanthanum complex was investigated. Lanthanum in the complex acts as a promoter of the catalyst [53].

A synergistic effect was observed in 1-octene hydroformylation using 13x zeolite-supported ruthenium/cobalt bimetallic catalysts. X-Ray photoelectron spectroscopy (XPS) and FTIR measurements indicate that this effect changes with cobalt loading. At high cobalt loading (2.4%), the synergistic effect involves mainly a dinuclear reductive elimination reaction between a cobalt acyl and ruthenium hydride $[HRu(CO)_4]^-$. At low cobalt loading (0.56%), the effect was explained by assuming an interaction between Co(0) and Ru(III) [54].

The phosphino-PVC-supported bromomethylidenetricobalt nonacarbonyl was found to show high activity and selectivity in hydroformylation at 40 bar. Thus the conversion of 1-heptene is almost 100% with an aldehyde selectivity of 94.3% or less at 140°C [55].

$RhCo_3(CO)_{12}/SiO_2$, after decarbonylation, was found to be regenerated under carbon monoxide, and catalyzes the hydroformylation of ethylene with high activity and stability [56]. The hydroformylation of methyl methacrylate, with a conversion of 95.6% and a selectivity of 92.8% for the normal product methyl β-formylisobutyrate, was achieved when the reaction was catalyzed by a silica-supported poly-γ-aminopropylsiloxane-rhodium/cobalt bimetallic complex. The catalyst was found to be stable during the reaction and could be used repeatedly [57].

Phosphites of varying molecular bulkiness were attached to styrene copolymers to prepare rhodium hydroformylation catalysts. The catalytic activity of the polystyrene-bonded system with the most bulky phosphite was identical to that of a low-molecular-weight analog. The catalysts showed high activity towards the hydroformylation of otherwise non-reactive cyclooctene [58].

Alkali metal salt-modified, supported, aqueous phase rhodium catalysts, prepared by a co-impregnation method using alkali metal chlorides, were found to be active and selective for olefin hydroformylation. Salt addition promoted the formation of aldehydes with high selectivity, the aldehyde yield being increased by more than 2.5-fold at the optimal salt to Rh ratio. Hydroformylation using the supported, aqueous phase rhodium catalysts under atmospheric pressure of CO/D_2 was about 1.3-fold faster than that under CO/H_2 [59].

The preparation of an organorhodium complex on smectite clay and its catalytic activity for the hydroformylation of vinylsilanes have been studied. Thus sodium montmorillonite reacts with the dimer of chloro(1,5-cyclooctadiene)rhodium(I) in dichloromethane to form a material (Rh/clay) in which rhodium is covalently attached to the silicate sheets of montmorillonite. Linear silylaldehydes were obtained as the major or only product in excellent yield by the hydroformylation of trialkylvinylsilanes or triphenylvinylsilane catalyzed by Rh/clay [60]. Two benzoyl-thiourea-functionalized silica xerogels, $4.5SiO_2 \cdot SiO_{3/2}(CH_2)_3NHC(S)NHC(O)Ph$ (XGbztu) and $SiO_{3/2}(CH_2)_3NHC(S)NHC(O)Ph$ (XGbztu*), were prepared from $(EtO)_3Si(CH_2)_3NHC(S)NHC(O)Ph$ by the sol–gel process. They can bind to rhodium(I) species giving the composite materials Rh/XGbztu and Rh/XGbztu*, which were found to be very active, insoluble and recoverable catalysts for the hydroformylation of styrene. The anchored species undergo major changes during the catalytic cycles, particularly in the Rh/XGbztu system, whose iso to normal selectivity ratio gradually increases in the first five runs [61].

Poly(styryl)bipyridine-supported $Rh_2(CO)_4Cl_2$ was found to be a good catalyst in the hydroformylation reaction of 1-heptene under 40 bar pressure of $CO/H_2 = 1/1$ [62].

The effects of the modification of Pd/SiO_2 on its catalytic activity in ethene hydroformylation were studied. In the case of modification with $Rh(OAc)_3$, the rate of propionaldehyde formation increased with increasing level of modification [63]. The hydroformylation of propene on Pd/SiO_2 and $(Pd + Ln)/SiO_2$ catalyst prepared from organometallic precursors has been studied. Based on the FTIR and temperature programmed desorption (TPD) spectra and the characteristic properties of the catalysts, it was suggested that propene hydroformylation on $(Pd + Ln)/SiO_2$ catalysts occurs on monometallic Pd clusters without the participation of the mixed bimetallic active sites and the active CO complexes formed on them [64].

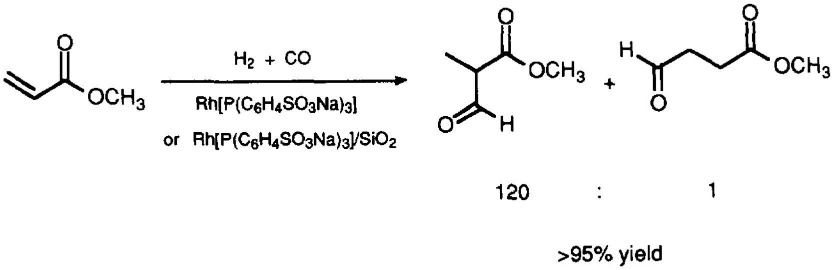
A number of linear and crosslinked polymer ligands containing P, N or S as donor atoms were prepared. The hydroformylation of olefins was carried out under mild conditions in the presence of catalysts prepared by the complexation of these ligands with various homogeneous complexes or metal salts. The observed results were explained in terms of the influence of the polymer matrix (or the structure and composition of the polymer chain) and the properties of the polymer/metal complexes on the activity and selectivity. The most important factor for enhancing the selectivity towards linear aldehydes lies in the properties of the polymer/metal complex. High selectivity (up to 95%) was obtained using polymeric phosphine ligand/Pt/Sn complexes as catalysts in the hydroformylation of olefins [65]. The hydroformylation of olefins using supported film catalysts has been studied [66] (see also Refs. [40,67].

1.2.2. Biphasic systems

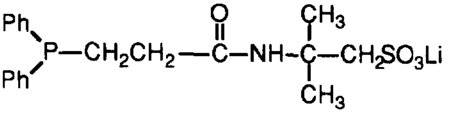
A novel concept for performing stoichiometric and catalytic chemical transformations has been developed based on the limited miscibility of partially or fully fluorinated compounds with non-fluorinated compounds. A fluorous biphasic system consists of a fluorous phase, containing a dissolved reagent or catalyst, and another phase, which may be any common organic or non-organic solvent with limited or no solubility in the fluorous phase. The chemical transformation may occur either in the fluorous phase or at the interface of the two phases. The application of fluorous biphasic systems has been demonstrated for the extraction of rhodium from toluene and for the hydroformylation of olefins [68].

A water-soluble disodium bis[8-(*p*-sulfonatophenyl)octyl][(−)-menthyl]-phosphine-rhodium catalyst was used for the hydroformylation of styrene under two-phase conditions. The catalyst shows high catalytic activity, but virtually no optical induction. Normal to branched ratios for the hydroformylation of styrene are in the range 0.35–0.5 [69].

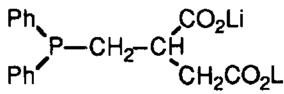
High activities and selectivities in the rhodium-catalyzed hydroformylation of methyl acrylate were reported using both two-phase and supported aqueous phase systems at 50 °C and 50 bar $CO/H_2 = 1/1$ [67].



The hydroformylation of methyl acrylate was studied in a two-phase (toluene/water) system in the presence of the water-soluble phosphines **20** and **21**. High yields and selectivities of methyl α-formylpropionate were obtained [70].


$Ph_2P{-}CH_2CH_2{-}C(=O){-}NH{-}C(CH_3)_2{-}CH_2SO_3Li$

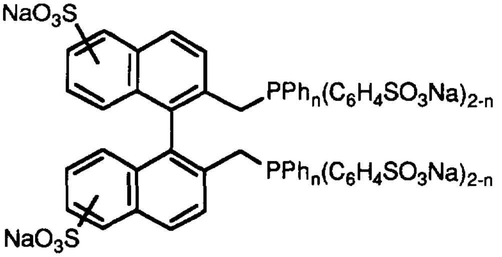
20


$Ph_2P{-}CH_2{-}CH(CO_2Li)CH_2CO_2Li$

21

Homologous ω-alkene carboxylic acid methyl esters were hydroformylated using the water-soluble rhodium-carbonyl/triphenylphosphine-*m*-trisulfonic acid sodium salt catalyst in an aqueous/organic two-phase system. The addition of cationic tensides, such as tetradecyl-trimethylammoniumbromide, was found to enhance the hydroformylation in the case of methyl 10-undecenoate [71]. Low- and medium-molecular-weight ω-unsaturated carboxylic acid methyl esters inclusive of the ω-decenoic acid ester were hydroformylated by a two-phase method in an aqueous/organic medium using the water-soluble complex $[HRh(CO)(PC_6H_4SO_3Na\text{-}m)_3]_3$ as catalyst. Higher molecular weight unsaturated fatty acid esters, e.g. the triple unsaturated linolenic acid methyl ester, or fatty oils, e.g. linseed oil, were hydroformylated only by the micellar two-phase technique in which surfactant micelles cause solubilization of the water-insoluble unsaturated fatty substances in the aqueous catalyst phase. An evaluation of the efficiency of various types of surfactant in micellar two-phase hydroformylation showed that cationic surfactants were the most suitable. Linoleic acid methyl ester was hydroformylated to the triformyl derivative with a selectivity of 55%. The recovery of the catalyst solution free from losses of rhodium was achieved by simple phase separation [72].

In the biphasic hydroformylation of propene, the sulfonated ligands **22** and **23** exhibited very high activities and productivities at low phosphine to rhodium ratios. Phosphine **22** led to a normal to iso ratio of 98 : 2 for the resulting butyraldehyde [73].



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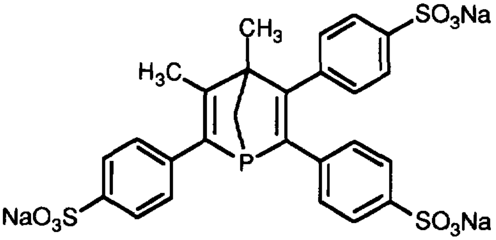
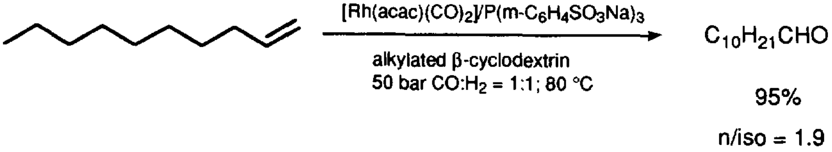


23

1-Hexene was hydroformylated in a two-phase system using the water-soluble catalysts $Rh_4(CO)_{12}$ with a mixture of 94% TFPPDS plus 6% TFPPTS and $Rh_4(CO)_{12}$ with TPPTS (TFPPDS, disodium salt of disulfonated tris(4-fluorophenyl)phosphine; TFPPTS, trisodium salt of trisulfonated tris(4-fluorophenyl)phosphine; TPPTS, trisodium salt of trisulfonated triphenylphosphine). At low P to Rh ratios, higher selectivities to linear aldehydes were achieved with Rh/TFPPDS+TFPPTS than with Rh/TPPTS. The Rh/TFPPDS+TFPPTS complex was quantitatively recovered by simple separation of the aqueous layer from the organic layer which contains the substrate and the products [74].

Hydroformylation of 1-octene was studied in a two-phase system using an $[RhCl(1,5\text{-COD})]_2$ complex catalyst and the trisodium salt of tri(*m*-sulfophenyl) phosphine as a water-soluble ligand. The reaction was carried out in a batch reactor at pressures between 15 and 25 bar and temperatures of 60 and 70 °C. Ethanol was added as a co-solvent to enhance the octene solubility in the aqueous phase, and a buffer solution of sodium carbonate and bicarbonate was used to eliminate the formation of acetals. The hydroformylation products were *n*-nonanal and 2-methyloctanal with a selectivity to linear aldehyde of about 80%. The reaction was found to be first order with respect to both octene and catalyst concentrations. The dependence on the carbon monoxide pressure was complex with an enhancement at low partial pressures and an inhibition at high pressures. The reaction rate increased with the dihydrogen partial pressure. A semiempirical kinetic model was used to describe the rate of the reaction [75]. The hydroformylation of 1-octene under two-phase reaction conditions, with rhodium catalysts derived from TPPTS or novel water-soluble phosphines $P[C_6H_4\text{-}p\text{-}(CH_2)_xC_6H_4\text{-}p\text{-}SO_3Na]_3$ ($x=3$, 6), was found to depend on the salt concentration. Both the reaction rate and reaction selectivity to the linear aldehyde were affected by the ionic strength of the aqueous reaction medium. The reaction selectivity increased with increasing ionic strength, while the catalyst activity was dependent on whether the phosphine was capable of forming micelles. The reaction rate increased with increasing ionic strength with the new surface-active phosphines. It was proposed that a high ionic strength stabilizes the complex, $HRh(CO)(TPPTS)_3$, in aqueous solution [76]. The catalysis at the interface of a two-phase system can be enhanced by using a "promoter ligand" which, although soluble in the organic phase, will bind to the organometallic catalyst and thus increase its concentration close to the interface in the aqueous phase. This approach was employed for the hydroformylation of 1-octene using a rhodium-based catalyst. A rate enhancement by a factor of 10–50 was observed by the introduction of the promoter ligand PPh_3 in the organic phase [77].

Up to 100% conversion and 95% aldehyde selectivity was achieved in the rhodium-catalyzed hydroformylation of 1-decene using a water/alkene two-phase system in the presence of partially methylated β-cyclodextrin [78].



The hydroformylation of 1-dodecene was catalyzed by the water-soluble rhodium complex, $RhCl(CO)(TPPTS)_2$, under atmospheric pressure of $CO/H_2=1/1$ in an aqueous/organic biphasic system. The influence of the reaction parameters (catalyst concentration, surfactant, pH of the aqueous phase, molar ratio of TPPTS to Rh and organic solvent) on the catalytic activity was investigated. The addition of the surfactant cetyltrimethylammonium bromide (CTAB) induced micelle formation, promoted liquid–liquid transport in the biphasic system and accelerated the hydroformylation of 1-dodecene [79].

The catalytic properties of water-soluble $RhCl(CO)(TPPTS)_2$ for the hydroformylation of long-chain olefins in a biphasic system in the presence of CTAB were studied. The influence of the reaction parameters, such as the temperature, total pressure, partial pressure ratio of CO to H_2 and molar ratio of TPPTS to Rh, was investigated. The addition of CTAB markedly accelerated the reaction rate. At 10 bar total pressure ($CO/H_2 = 1/1$), 100 °C and a TPPTS to Rh ratio of 16, the turnover frequencies for the hydroformylation of 1-hexene, 1-octene and 1-dodecene were 39.8, 38.8 and 37.5 min^{-1} respectively. The ratio of branched aldehyde to normal aldehyde was 3.6 or more [80].

The non-ionic, water-soluble phosphines, tris[*o*-[(polyoxyethylene)oxy]phenyl]-phosphine and tris[*p*-[(polyoxyethylene)oxy]phenyl]phosphine were prepared, and their rhodium complexes were used as catalysts in a two-phase system for the hydroformylation of olefins. The catalysts show good activity and selectivity. At 100 °C and 60 bar total pressure of $CO/H_2 = 1/1$, the conversion of 1-dodecene and the selectivity to aldehyde were better than 85%. The effects of the reaction conditions on the hydroformylation were examined [81] (see also Ref. [23]).

1.2.3. Metal catalysts

Bimetallic catalysts containing ruthenium and iron on SiO_2 and carbon supports were found to be catalytically active in the formation of C_4 aldehydes and alcohols in the hydroformylation of propylene at 166 °C and 2 bar of $CO/H_2/C_3H_6$ (1/1/1). The addition of iron to ruthenium alters the activity of the monometallic ruthenium catalyst and favors the hydrogenation of CO to methanol [82].

The hydroformylation of 1,3-butadiene, 2-methyl-1,3-butadiene and 1,3-pentadiene using rhodium vapor/mesitylene co-condensates as catalytic precursor has been reported. The reaction gives β,γ-unsaturated monoaldehydes with high chemoselectivity and regioselectivity. η^3-Butenyl complexes, derived from the addition of Rh–H species to the conjugated double bond system, are likely intermediates, as suggested by deuterioformylation experiments [83].

The complex kinetic influence of surface catalyst species was discussed for propene hydrogenation and hydroformylation over silica-supported palladium catalysts [84].

2. Hydroformylation-related reactions of Co

2.1. Ketone formation

Ketone formation was observed during ethylene hydroformylation over sulfided rhodium, iridium and nickel/molybdenum carbon-supported catalysts [85]. High-resolution ^1H, ^{13}C and ^{31}P NMR were used for step-by-step investigation of ethylene hydrocarbonylation into diethyl ketone in the P_2PtX_2(or P_4Pt)/CF_3COOH/H_2O ($P \equiv PPh_3$; $X \equiv CF_3COO^-$; $[H_2O] \leq 30$ vol.%) catalytic system. Key Pt(II) intermediates were identified and characterized, and in addition their reactivity was studied [86].

2.2. Homologation

C_n formates $HCO_2C_nH_{2n+1}$ ($n = 1$–5) can be catalytically converted to C_{n+1} alcohols $C_nH_{2n+1}CH_2OH$ and their esters in the presence of a cobalt catalyst and, optionally, a ruthenium compound. The reaction occurs under modest CO pressure in the presence of lithium iodide and tributylphosphine. It is promoted by an onium salt. The reaction is highly selective with respect to the formation of the next higher homolog. The method is general and permits homologation of alkyl groups other than methyl, although turnovers are sharply decreased with increasing chain length of the alkyl group. The reaction occurs via a complex pathway different from typical mechanisms previously proposed for the hydrocarbonylation of methanol and higher alcohols [87].

In the presence of the homogeneous Rh/Cr/I catalyst system, methyl formate can be isomerized to acetic acid under carbon monoxide pressure with high conversion rates and excellent selectivity. It was suggested that the formation of acetic acid proceeds via the rate-determining carbonylation of the ester to the mixed anhydride of formic acid and acetic acid, followed by decomposition to acetic acid and carbon monoxide [88] (see also Ref. [51]).

2.3. *Hydroesterification*

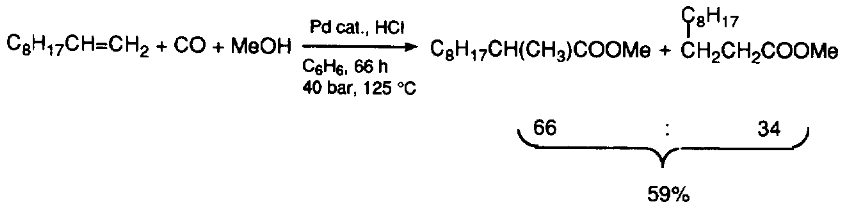
Palladium acetate immobilized on montmorillonite was found to be an efficient catalyst for the hydroesterification of olefins with carbon monoxide and methanol in the presence of triphenylphosphine and an acid promoter, affording branched chain esters. The reaction is regiospecific for aryl olefins and vinyl benzoate and regioselective for aliphatic olefins [89], e.g.

$$\mathrm{PhCH{=}CH_2 + CO + MeOH \xrightarrow[\substack{C_6H_6,\ 24\ h \\ 40\ bar,\ 125\ ^\circ C}]{Pd\ cat.,\ HCl} PhCH(CH_3)COOMe}$$

94%

$$\mathrm{PhCOOCH{=}CH_2 + CO + MeOH \xrightarrow[\substack{C_6H_6,\ 48\ h \\ 40\ bar,\ 125\ ^\circ C}]{Pd\ cat.,\ HCl} PhCOOCH(CH_3)COOMe}$$

71%



$$\mathrm{C_8H_{17}CH{=}CH_2 + CO + MeOH \xrightarrow[\substack{C_6H_6,\ 66\ h \\ 40\ bar,\ 125\ ^\circ C}]{Pd\ cat.,\ HCl} \underbrace{C_8H_{17}CH(CH_3)COOMe + \overset{C_8H_{17}}{\overset{|}{C}}H_2CH_2COOMe}_{\substack{66\ :\ 34 \\ 59\%}}}$$

The effects of promoters and reaction conditions on the selectivity of the palladium complex-catalyzed hydrocarbalkoxylation of 4-methylstyrene were studied. The catalyst system $\mathrm{PdCl_2/CuCl_2/PPh_3}$ dissolved in a non-polar solvent was found to provide a nearly regiospecific conversion to the branched acid ester at high rates at 100 °C and 41 bar carbon monoxide pressure. The observed dependence of the regioselectivity on monodentate vs. bidentate ligands led to the suggestion that the key catalytic species may be a palladium hydride complex rather than a carbalkoxy complex [90].

Dimethyl malonate was obtained in up to 75% yield by methoxycarbonylation of dichloromethane in methanol/methyl formate medium in the presence of electrogenerated $[Co(CO)_3PBu_3]^-$ catalyst [91]. Reactive chlorides, such as $PhCH_2Cl$, $CH_3OC(O)CH_2Cl$ and $NCCH_2Cl$, were carbonylated into esters with methyl formate as the sole source of carbon monoxide and methanol, the tetracarbonyl cobaltate anion as the catalyst and sodium carbonate as the base [92], e.g.

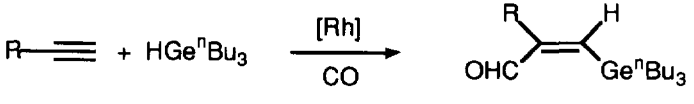
$$PhCH_2Cl + HCOOCH_3 \xrightarrow[60\ ^{o}C,\ Na_2CO_3,\ 15\ h]{Na[Co(CO)_4],\ CO\ 13\ bar} PhCH_2COOCH_3$$

(97% yield at 97% conversion)

The complex cis-$[\overline{RhI(CO)(Ph_2PCH_2P(S})Ph_2]$ was found to be eight times more active than the classic Monsanto catalyst $[RhI_2(CO)_2]^-$ for the carbonylation of methanol at 180 °C [93].

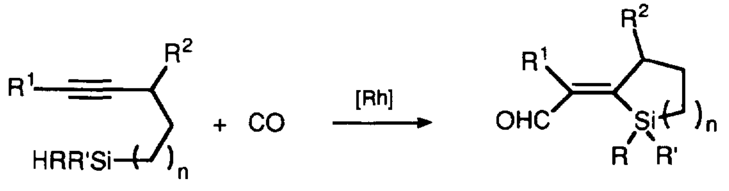
2.4. Germylformylation, silylformylation and thioformylation

The zwitterionic rhodium complex $[\eta^6\text{-}C_6H_5BPh_3]^-[Rh(COD)]^+$ was found to catalyze the germylformylation of terminal alkynes at 90 °C and 20 bar in methylene chloride [94], e.g.



R = ^{n}Bu, 2-Bu, ^{i}Bu, Ph(CH$_2$)$_3$, Ph, HOCH$_2$ 66-82%

Alkenyldiorganylsilanes **24** were found to undergo intramolecular silylformylation reactions on exposure to carbon monoxide in the presence of either the zwitterionic rhodium complex $[\eta^6\text{-}C_6H_5BPh_3]^-[Rh(COD)]^+$ or $Rh_4(CO)_{12}$ and triethylamine. In the totally regiospecific and stereospecific reaction, aldehydes **25** are formed in 37%–83% isolated yield [95].

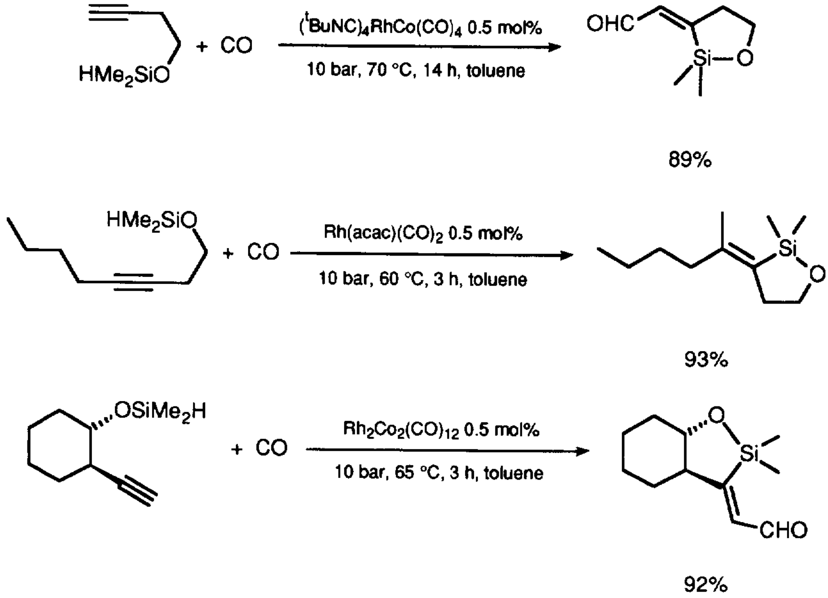


24

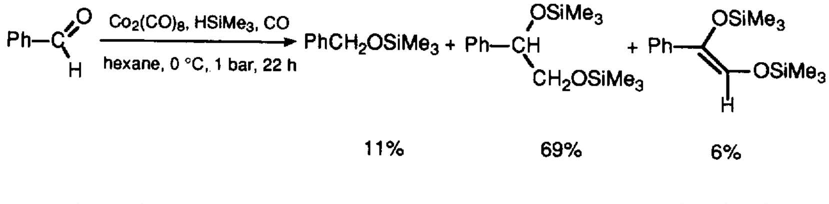
n = 1,2; R^1 = H, Et, ^{n}Bu, Ph
R^2 = H, Me
R, R' = Me, Ph

25

The intramolecular silylformylation of ω-(dimethylsiloxy)-alkynes catalyzed by rhodium and rhodium/cobalt complexes has been investigated and complete regioselectivity was found [96], e.g.

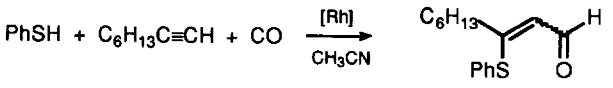


The octacarbonyldicobalt-catalyzed reaction of aromatic aldehydes with hydrosilanes and carbon monoxide (1 bar) was found to result in the incorporation of CO into the carbonyl carbon atom of aldehydes to give arylethane-1,2-diol disilyl ethers as the main product. The reaction of aliphatic aldehydes gives similar products, but with low yields [97].

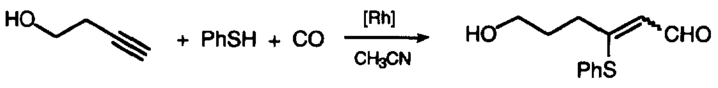


The reaction of oxetanes with hydrosilane and carbon monoxide in the presence of $[RhCl(CO)_2]_2$-amine as catalyst was found to result in ring-opening silylformylation to give γ-siloxy aldehydes, such as $PhMe_2SiO(CH_2)_3CHO$, in 42%–83% yield. The addition of amines is essential for silylformylation to proceed, and 1-methylpyrazole was found to be the most effective of the amines examined. The ring opening of 2-alkoxyetanes occurs predominantly at the primary carbon atom with a regioselectivity of 95% [98].

The first transition metal-catalyzed thioformylation of terminal acetylenes with carbon monoxide and thiols has been reported. Rhodium(I) complexes bearing phosphine ligands were found to be excellent catalysts with $RhH(CO)(PPh_3)_3$ being the most effective. Thus the reaction of 1-octyne with benzenethiol and carbon monoxide (30 bar) in the presence of 3 mol.% of $RhH(CO)(PPh_3)_3$ at 120 °C for 5 h gives an isolated yield of 82% of **26** with an *E*/*Z* ratio of 13 : 87. A similar yield, but a reverse *E*/*Z* ratio of 86 : 14, was observed in the case of **27** [99].



26



27

76% yield

2.5. *Water–gas shift reaction*

The kinetics and mechanism of metal carbonyl catalysis of carbon monoxide and formate reactions were studied. The water–gas shift reaction was found to be catalyzed by aqueous metal carbonyl systems derived from mononuclear carbonyls, such as $Fe(CO)_5$ and $M(CO)_6$ ($M \equiv Cr$, Mo and W), and bases in the 140–200 °C temperature range. The water–gas shift reaction in basic methanol/water solution containing $Fe(CO)_5$ is first order in $[Fe(CO)_5]$, zero order in [CO] and essentially independent of the base concentration, and appears to involve an associative mechanism with a metallocarboxylate intermediate $[(OC)_4Fe{-}CO_2H]^-$. The water–gas shift reactions using $M(CO)_6$ as catalyst precursors are first order in $[M(CO)_6]$, inverse first order in [CO] and first order in $[HCO_2^-]$, and appear to involve a dissociative mechanism with formatometallate intermediates $[(OC)_5M{-}OCHO]^-$. The Reppe hydroformylation of ethylene to produce propionaldehyde and 1-propanol in basic solution containing $Fe(CO)_5$ occurs at 110–140 °C. This reaction is second order in $[Fe(CO)_5]$, first order in $[C_2H_4]$ up to a saturation pressure greater than 15 bar and inhibited by CO. These experimental results suggest a mechanism in which the rate-determining step involves a binuclear iron carbonyl intermediate [100].

The kinetics of the homogeneous water–gas shift reaction in the presence of $Ru_3(CO)_{12}$ in acidic aqueous diglyme solution were studied at moderate temperature and CO pressure using a continuous flow-stirred reactor. The turnover frequency value (mole of CO_2 per mole of $Ru_3(CO)_{12}$ per 24 h) of carbon dioxide production was found to be 7.1 for $[Ru_3(CO)_{12}]=4.7\times10^{-3}$ M, $[H_2O]=3.5$ M, $[H_2SO_4]=0.25$ M in diglyme, $P_{CO}=0.9$ bar and $T=100$ °C. The kinetics of the reaction showed a first-order dependence on the carbon monoxide pressure over the range 0.3–0.9 bar, an inverse dependence on the sulfuric acid concentration over the range 0.25–1.0 M, a non-linear dependence on the water concentration over the range 2.0–9.6 M and a second-order dependence on the ruthenium concentration over the range 1.56–4.69 mM. These results have been interpreted on the basis that the predominant species under the reaction conditions is $[HRu_2(CO)_{9-x}(\text{diglyme})_x]^+$ ($x \geq 3$) [101].

The catalytic activity of $Ru_3(CO)_9L_3$ (L ≡ arylphosphine) in the water–gas shift reaction and in the reduction of nitro derivatives to amines was studied [102]. The use of sodium cobalt tetracarbonyl and cobalt acetate plus alkali as precursors for coal liquefaction involving CO/H_2O or H_2 was investigated [103]. Homogeneous catalysis of the water–gas shift reaction by *cis*-$[Rh(CO)_2(\text{amine})_2]PF_6$ complexes (amine ≡ 4-picoline, pyridine, 3,5-lutidine and 2,6-lutidine) in aqueous acetonitrile solutions was reported [104] (see also Refs. [105,106]).

2.6. Reduction of CO and CO_2

The catalytic activities of the heterobinuclear complexes (dppe)Rh(μ-CO)$_2$M(CO)$_3$ (M ≡ Cr, Mo, W) for CO hydrogenation were studied [107]. Cobalt-based Ziegler-type catalysts have been used at 200 °C and 1 bar pressure ($H_2/CO = 2/1$) for the catalytic hydrogenation of carbon monoxide [108].

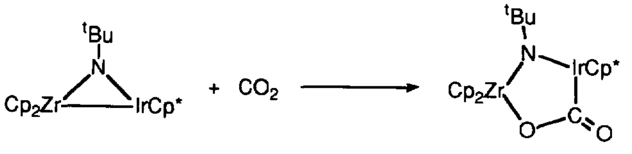
The hydrogenolysis of methyl formate to methanol, as the second step of the low-temperature methanol synthesis from syngas, was studied using rhenium catalysts. "Rhenium blacks" containing reduced Re (0) species, produced in situ starting from soluble rhenium precursors such as Re_2O_7 or $Re_2(CO)_{10}$, were found to be active and selective (99%) in the hydrogenation of the formyl group to methanol [109].

The catalytic behavior of an SiO_2-supported $HRh(\text{dppe})_2$ catalyst for CO hydrogenation to give C_{1-2} alcohols and for the hydroformylation of propene to give butyraldehyde was reported [38].

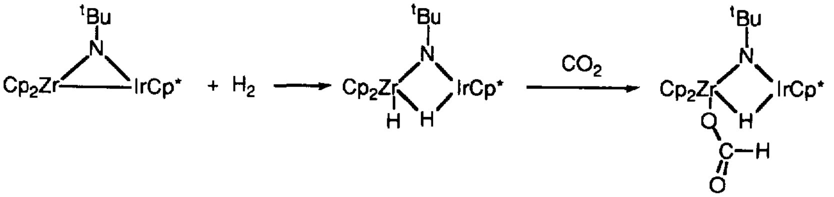
The early–late heterobinuclear complex $Cp_2Zr(\mu\text{-N}^t\text{Bu})IrCp^*$ (Cp, cyclopentadienyl; Cp*, pentamethylcyclopentadienyl) was found to react with CO_2 by direct addition of a carbon dioxide C=O bond across the Zr–Ir bond, leading to the unique simple heterobimetallacyclic complex **28**. CO_2 reacts with the dihydride complex **29** leading to a heterobimetallic formato complex **30** in 75% yield, which can be converted stoichiometrically to formic acid [110].

An $Fe_3(CO)_{12}$ catalyst supported on zeolite ZSM-5 was found to exhibit high catalytic activity for the hydrogenation of carbon dioxide and gives a high selectivity for light olefins. The formation of ethene takes place effectively at a temperature of approximately 240–280 °C [111].

In the presence of ethylene oxide, CO_2 was efficiently hydrogenated at 140 °C and 80 bar in 1-methylpyrrolidine as solvent to give CO and ethylene glycol in about 80% yield using $RuCl_2(PPh_3)_2$ as the catalyst precursor. The participation of ruthenium carboxylate, carbonyl and dihydrido complexes was suggested in the catalytic cycle [112]. The ruthenium complex $[Ru(\text{bpy})_2(\text{quinoline})(CO)]^{2+}$ was found to catalyze the reductive disproportionation of CO_2 to afford CO and CO_3^{2-} in the electrochemical reduction of CO_2 in the presence of $LiBF_4$. The same reduction in the presence of $(CH_3)_4NBF_4$ in DMSO/MeCN produced CH_3COCH_3, $CH_3COCH_2COO^-$ and $HCOO^-$ as well as CO and CO_3^{2-} [113]. The homogeneous



28

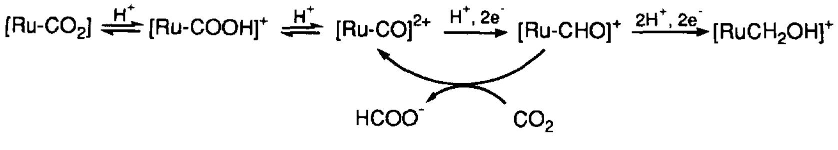


29 **30**

ruthenium-catalyzed hydrogenation of supercritical carbon dioxide in the presence of methanol at 80 °C, $P_{H2} = 80$ bar and $P_{CO2} = 120–130$ bar was found to yield methyl formate at up to 3500 mol (mol catalyst)$^{-1}$, which is one order of magnitude greater than the most efficient system at any temperature [114].

Carbon dioxide is homogeneously hydrogenated to methanol using $Ru_3(CO)_{12}$ as the catalyst precursor in the presence of iodide (KI) in 1-methyl-2-pyrrolidinone solution at 240 °C [115].

The ruthenium complex $[Ru(bpy)(trpy)(CHO)]^+$ (bpy, 2,2′-bipyridine; trpy, 2,2′:6′,2″-terpyridine) was identified as a key intermediate in four- and six-electron reductions of CO_2 producing HCHO, CH_3OH, HOOCCHO and $HOOCCH_2OH$. A new pathway of HCOOH formation in electrochemical CO_2 reduction was suggested [116].



The molecular structures and reactivities of several ruthenium mono(bipyridine) carbonyl compounds were studied as possible models of intermediates in water–gas shift reactions and in CO_2 reduction processes [105]. The 6,6′-dichloro-2,2′-bipyridine complex of ruthenium, *cis*-$[Ru(6,6'\text{-}Cl_2bpy)_2(H_2O)_2](CF_3SO_3)_2$, in ethanol and in the presence of Et_3N was found to be a very effective catalyst for the hydrogenation of CO_2 to HCO_2H. The HCO_2H thus produced formed a salt or an adduct with the amine. Yields of up to 5000 mol (mol ruthenium)$^{-1}$ can be achieved. In the absence of Et_3N, the product is ethyl formate and the turnover number is much lower [117].

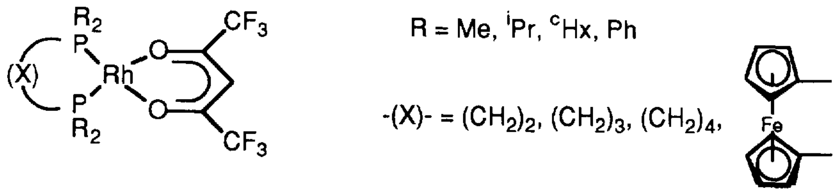
Reaction of $C_5Me_5Ru(P^cHx_3)Cl$ with 1–2 bar CO_2 in the presence of $NaBH_4$ was found to give formic acid. Deuterium labeling experiments suggest that the acid proton of formic acid comes from the solvent [118].

Rhodium(I) carbonyl and ruthenium(II) complexes with the water-soluble phosphines 1,3,5-triaza-7-phospha-tricyclo[3.3.1.1^{3,7}]decane, tris(hydroxymethyl)phosphine and tris(2-cyanoethyl)phosphine were found to be catalysts for the water–gas shift reaction and the reduction of CO_2 leading to the formation of CO and CH_4 [106].

The tetrahydride tricobalt cluster $Cp_3^*Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$ was found to reduce CO_2 at 5 bar pressure and 120 °C to form the dicobalt dicarbonyl complex $[Cp^*Co(\mu\text{-}CO)]_2$ in 45% yield by ^1H NMR [119].

Carboxylic acids RCOOH (R ≡ Me, Et, Ph) were catalytically produced from carbon dioxide, dihydrogen and the corresponding organic iodides at 80 bar $CO_2/H_2 = 1/3$ and 240 °C in 1-methylpyrrolidine in the presence of the bimetallic catalyst $Ru_3(CO)_{12}/Co_2(CO)_8$ or $Ni(COD)_2/Co_2(CO)_8$ [120].

The hydrogenation of CO_2 to formic acid, catalyzed by $HRh(PH_3)_2$ as a model system, has been investigated using ab initio MO/MP2 calculations [121]. Rhodium(III) was found to be an active homogeneous catalyst in the presence of NO_2^- for the decomposition of HCO_2H to H_2 and CO_2 in aqueous solution at 90 °C. Experiments at different rhodium concentrations indicate that this reaction is approximately pseudo-first order in [Rh], suggesting that mononuclear nitrorhodium complexes are the catalytically active species [122]. Rhodium complexes **31** were found to be very effective catalyst precursors for the catalytic hydrogenation of CO_2 to formic acid in dimethylsulfoxide/triethylamine (5/1) solvent at 40 bar and 25 °C. The highest turnover frequency of 1335 h^{-1} was observed in the case of R ≡ cyclohexyl and X ≡ $(CH_2)_4$ [123].



31

The metal sulfide clusters $[\{Ir(C_5Me_5)\}_3(\mu^3\text{-}S)_2]^{2+}$ and $[\{Co(C_5H_4Me)\}_3(\mu^3\text{-}S)_2]^{2+}$ were found to catalyze the electrochemical CO_2 reduction to produce selectively oxalate at −1.30 and −0.70 V (vs. Ag/AgCl) respectively in acetonitrile [124]. Nickel(II) complexes of 1,4,7,11-tetraazacyclotetradecane (isocyclam) were found to be good electrocatalysts for the two-electron reduction of CO_2 to CO, but not as efficient as $[Ni(cyclam)]^{2+}$ [125].

A dinuclear palladium complex containing a bridging hexaphosphine ligand, $[Pd_2(CH_3CN)_2(eHTP)](BF_4)_4$ (eHTP, $(Et_2PCH_2CH_2)_2PCH_2P(CH_2CH_2PEt_2)_2$), was found to catalyze the electrochemical reduction of CO_2 to CO in acidic dimethylformamide solutions [126] (see also Refs. [42,82]).

3. Reviews

(1) Synthesis of perfumery aldehydes by hydroformylation. The hydroformylation of various terpenes and related molecules under mild conditions has been reviewed (seven references) [127].

(2) Recent advances in hydroformylation catalyzed by water-soluble transition metal complexes in two-phase systems. A review with 36 references on the synthesis and application of water-soluble phosphines and their transition metal complexes in aqueous/organic solvent two-phase system catalytic hydroformylation [128].

(3) Asymmetric hydroformylation of prochiral olefins to produce optically active aldehydes (a review with 26 references) [129].

(4) A new approach in asymmetric hydroformylation. A review with five references on optically active phosphinephosphite-ruthenium(I) complex catalysts for asymmetric hydroformylation [130].

(5) The asymmetric hydroformylation of alkenes catalyzed by complexes of rhodium, cobalt, platinum, ruthenium and palladium was reviewed (47 references) [131].

(6) The deactivation of rhodium hydroformylation catalysts and their methods of regeneration have been reviewed (35 references) [132].

(7) Facile catalyst separation without water: fluorous biphasic hydroformylation of olefins. A review of the research by I.T. Horváth and J. Rábai with commentary (10 references) [133].

(8) Hydroformylation of olefins with rhodium complexes. A review with 280 references [134].

(9) New ways of homogeneous biphasic catalysis in hydrogenation and hydroformylation. A review with 15 references [135].

(10) Recent advances in enantioselective hydroformylation. A review with 77 references [136].

(11) Asymmetric hydroformylation. A review of palladium-, platinum- and rhodium-catalyzed systems with approximately 150 references [137].

(12) Introducing water-soluble triphenylphosphine trisulfonate and related ligands for industrial biphasic processes. A review with more than 65 references [138].

(13) Progress in hydroformylation and carbonylation. A review about the last 15 years of hydroformylation and carbonylation chemistry, including technical and commercial aspects, with more than 522 references [139].

(14) Rhodium and platinum complexes in homogeneous reactions and asymmetric syntheses. A review with more than 50 references [140].

(15) Photocatalysis. Mechanistic studies of the homogeneous photochemical water–gas shift reaction catalyzed under mild conditions by novel cationic iridium(III) complexes (13 references) [141].

(16) Carbonyl clusters of transition metals on oxide supports as heterogeneous catalysts for hydrocarbon synthesis. A review with 55 references of the methods of preparation of heterogeneous catalysts by the immobilization of carbonyl clusters of transition metals on oxide supports, as well as the study of the state

of supported compounds and their catalytic properties in CO hydrogenation and olefin hydroformylation [142].

(17) The preparation of hydrocarbons and oxygen-containing compounds from CO, H_2 and 3d components was reviewed (20 references) [143].

(18) Homogeneous hydrogenation of carbon dioxide. A review with 132 references [144].

(19) Carbon dioxide as a raw material. A review of the catalytic reduction of CO_2 to formic acid and its derivatives (electrocatalytic, photochemical and homogeneous transition metal-catalyzed reactions) (100 references) [145].

(20) Homogeneous hydrogenation of carbon dioxide with transition metal complexes. A review with 67 references of the coordination chemistry of carbon dioxide, homogeneous catalytic hydrogenation of carbon dioxide with transition metal complexes and reduction of carbon monoxide in supercritical fluids [146].

The metals and their associated references are given in Table 1.

Table 1
Metal index

Metal	Reference
Zr	[110]
Ln	[53,64]
Cr	[88,100,107]
Mo	[85,100,107]
W	[100,107]
Mn	[39]
Re	[109]
Fe	[82,100,111]
Ru	[40–44,51–54,82,87,101,102,105,106,112–118,120,131]
Co	[1–7,54–57,91,92,96,97,103,108,119,120,124,131]
Rh	[5,7–38,46,56–63,67–81,83,85,88,93–96,98,99,104,106,107,121–123,131,134,137,140]
Ir	[85,110,124,141]
Ni	[85,120,125]
Pd	[63,64,84,89,90,126,131,137]
Pt	[37,47–50,65,86,131,137,140]
Cu	[90]

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