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Review

Application of transition metals in hydroformylation annual survey covering the year 2004

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

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Contents

Abstract

Hydroformylation in homogeneous and heterogeneous systems, and hydroformylation related reactions of carbon monoxide reported in 2004 are reviewed.

Keywords: Hydroformylation; Silylformylation; Hydroxycarbonylation; Alkoxycarbonylation; Hydroaminomethylation; Water–gas shift reaction; Reduction of carbon dioxide; Transition metals

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* Tel.: +36 88 624 156; fax: +36 88 624 469.
E-mail address: ungvary@almos.vein.hu.

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1. Hydroformylation

1.1. Homogeneous systems

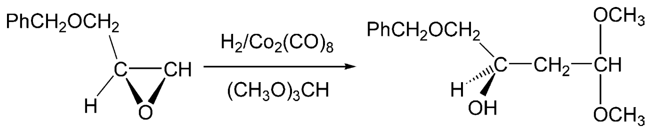
1.1.1. Cobalt catalysts

A cobalt carbonyl carbene dimer, $Co_2(CO)_6(IMes)_2$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), was tested as a catalyst for the hydroformylation of 1-octene. At 85 bar, H_2:CO = 2:1 pressure and 170 °C, no hydroformylation products were obtained [1].

The $HCo(CO)_3$-catalyzed acetylene hydroformylation reaction has been investigated with the B3LYP density functional method. It was found that acetylene hydroformylation for producing unsaturated aldehyde takes place along a pathway similar to that for olefins [2].

The carbonylation reaction of propylene oxide in the presence of various $[\text{Lewis acid}]^+[Co(CO)_4]^-$ salts was investigated using in situ ATR-IR spectroscopy. β-Alkoxy-acylcobalttetracarbonyl species were found to be key intermediates from which two reaction routes start depending on the Lewis acid used. Labile Lewis acid–alkoxy combinations favor producing primarily lactone products [3].

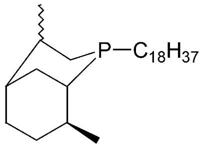
A wide range of epoxides were efficiently converted to protected aldols by hydroformylation–acetalization reaction using $Co_2(CO)_8$ as a catalyst in trimethyl orthoformate. The formylation of terminal epoxides was found to be regioselective for the terminal position [4]. For example:



The reaction of olefins (1-octene, 3,3-dimethylbutene, cyclohexene) introduced to a pre-equilibrated $Co_2(CO)_8 + H_2$ system has been investigated by high pressure infrared spectroscopy. Based on the observed induction period for the formation of the corresponding aldehyde, the decrease in concentration of $HCo(CO)_4$ and increase in the concentration of $Co_2(CO)_8$ during the induction period, an active catalytic species of the type $H_xCo_y(CO)_z$ has been proposed [5]. Experiments with isotope mixtures of H_2/D_2 in the gas phase during the various steps of the reaction showed that the ratio of H/D isotopes in the hydrocarbon portion of the aldehyde product correlates with the $HCo(CO)_4/DCo(CO)_4$ ratio in solution, while the RC(=O)H/RC(=O)D product ratio correlates with the H_2/D_2 in the gas phase. It was concluded that the dominant pathway for the hydrogenolysis step in this type of hydroformylation is the direct reaction of hydrogen or deuterium with the acyl complex intermediate [6].

The effect of argon (280 bar) on the rate of aldehyde formation in 1-hexene hydroformylation catalyzed by $Co_2(CO)_8$ at 50 °C, 70 bar P(CO) and 85 bar $P(H_2)$ in toluene has been investigated by high-pressure FTIR spectroscopy. The initial rate of the reaction was found to be reduced by the presence of argon. A similar effect was observed in the $RhH(CO)(PPh_3)_3$-catalyzed cyclohexene hydroformylation reaction [7].

The phosphane-modified cobalt-catalyzed hydroformylation of 1-dodecene was investigated using **1** and **2** as the modifier. The composition of the cobalt species in the reaction mixture was deduced from high-pressure IR and NMR spectra [8].



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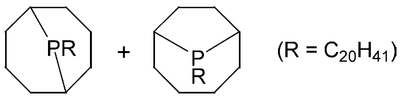

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The modified cobalt-catalyzed 1-octene hydroformylation using limonene-derived phosphanes was investigated at 170 °C and 85 bar H_2:CO = 2:1. The composition of the cobalt complexes in the reaction mixtures was deduced from IR and NMR spectra and correlated with the products of the hydroformylation reaction [9].

The composition of the cobalt complexes in supercritical carbon dioxide derived from $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ under hydroformylation conditions has been investigated by in situ high-pressure NMR spectroscopy. It was found that the phosphane-modified catalyst system is stable under low carbon monoxide pressures and the hydroformylation reactions can be carried out at low pressures. ^{31}P and ^{59}Co NMR spectra of the solution show that $HCo(CO)_3[P(p\text{-}CF_3C_6H_4)_3]$ and $HCo(CO)_2[P(p\text{-}CF_3C_6H_4)_3]_2$ are the only hydrido cobalt complexes present in detectable concentrations in $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$-catalyzed hydroformylation reactions [10].

The hydroformylation of 1-pentene and the composition of the cobalt complexes in the reaction mixture were studied at temperatures in the range 120–210 °C and pressures between 34 and 80 bar using $Co_2(CO)_6[P(OPh)_3]_2$ as the catalyst precursor. High-pressure IR and NMR spectra revealed the presence of various hydrido-cobalt species [11].

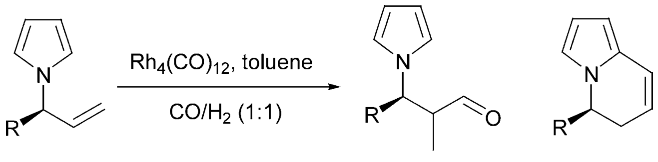
See also Ref. [58].

1.1.2. Rhodium catalysts

A theoretical investigation on the regio- and stereoselective outcomes of the hydroformylation reaction with an unmodified rhodium catalyst was carried out at the B3LYP/SBK(d) level on (1-vinyloxy-ethyl)-benzene and (1-methyl-but-3-enyl)-benzene. The theoretical results obtained are in good agreement with the experimental observations [12]. Ethylene hydroformylation catalyzed by phosphanerhodium complexes was computed by means of the density functional theory at the B3LYP/6-31G(d,p) level (Rh and P were at the LANL2DZ + polar basis set). The structures of the intermediates, the transition states, and the products were optimized [13]. A theoretical investigation of solvent effects on hydroformylation was carried out at the B3LYP/6-31G(d,p) level (LANL2DZ + polar for Rh and P) [14].

Algebraic system identification has been applied to the rhodium-catalyzed hydroformylation of alkenes using in situ FTIR spectroscopy [15].

Hydroformylation of (3*R*)-3-(pyrrol-1-yl)alk-1-enes (**3**) in the presence of $Rh_4(CO)_{12}$ at 100–125 °C and 30–100 bar $CO:H_2 = 1:1$ gave a mixture of **4** and **5** [16].



3 (R = Me, ^{i}Pr, ^{n}Pr) **4** **5**

Deuterioformylation of 1-phenyl-1-(*n*-pyridyl)-ethenes in the presence of a phosphane-modified $Rh_4(CO)_{12}$ catalyst was carried out at 100 bar of $CO:D_2 = 1:1$ and 80 °C at partial substrate conversion. Based on direct ^2H NMR analysis of the crude reaction mixture it was concluded that the branched alkyl rhodium intermediate is almost exclusively formed [17].

The catalytic activity of [Rh{*rac*-$CpCO_2(CHPh)_2OH$}(NBD)] and (−)-[Rh{(2*S*,3*S*)-$CpCO_2(CHPh)_2OH$}(NBD)] in the hydroformylation of 1-hexene and styrene was investigated and compared with that of [Rh{$CpCO_2$-$(CHR)_2OH$}(NBD)] (R = H, Me) [18].

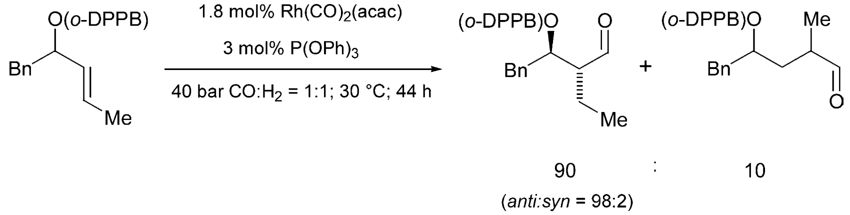
Dinuclear aryloxide- and carboxylate-bridged rhodium complexes were tested as catalysts in the hydroformylation of styrene and 1-octene. A regioselectivity towards the branched aldehyde up to 97 and 45%, respectively, was found [19]. A cationic rhodium(I) complex with hemilabile amino- and sulfur-containing phosphinite ligand was found to be efficient catalyst for the hydroformylation of styrene [20].

The homogeneous hydroformylation of 1-octene using an unmodified rhodium catalyst from a $Rh(CO)_2(acac)$ precursor was investigated in CO_2-expanded solvent media. At temperatures of 30 and 60 °C, the turnover numbers for aldehyde formation in CO_2-expanded acetone were found to be up to four-fold higher than those obtained in either neat acetone or compressed CO_2 [21]. Hydroformylation of styrene was studied in supercritical CO_2 using soluble rhodium catalysts, bound to a fluoroacrylate copolymer backbone through phosphine ligands. Conversions up to almost 100% and branched aldehyde selectivities of 95–100% were obtained [22]. The rhodium-catalyzed hydroformylation of 1,5-hexadiene and 1,7-octadiene to corresponding dialdehydes was investigated in compressed CO_2 and in toluene using different fluorinated phosphine compounds as ligands. The rhodium complex with tris(3,5-bis(trifluoromethyl)phenyl)phosphine was found to be highly effective in compressed CO_2 for double hydroformylation [23,24]. The hydroformylation of propene in the solvent mixture of supercritical CO_2 and water was investigated using a catalyst prepared from $Rh(CO)_2(acac)$ and TPPTS. Under the optimal reaction conditions 190–205 h^{-1} turnover frequency and a 4,4 *n*-butyraldehyde to isobutyraldehyde product ratio was found [25].

The hydroformylation of the water-soluble substrates, 4-penten-1-ol and 3-buten-1-ol in aqueous solution using $HRh(CO)(TPPTS)_3$ as the catalyst, was investigated. Activation parameters and reaction selectivity for the hydroformylation of 4-penten-1-ol were found to be dependent on solution ionic strength. As sodium sulfate was added the activation energy increased. The linear–branched selectivity was strongly influenced by the ionic strength and temperature. The reaction could be directed to yield a product distribution of modest linearity (75%) or an exceptionally high ratio of the branched product (98%) as a cyclic 2-hydroxy-3-methyltetrahydropyran [26].

A catalyst formed from $RhCl_3{\cdot}3H_2O$ precursor in triethyl orthoformate solution was found to show high activity in the hydroformylation reaction of various alkenes. The addition of triphenyl phosphite to this catalytic system increased the selectivity towards the branched aldehydes with aryl alkenes [27].

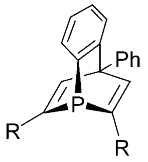
High regio- and stereoselectivity was achieved in rhodium-catalyzed *ortho*-diphenylphosphanylbenzoate (*o*-DPPB)-directed hydroformylation reactions of various 1,3-disubstituted and mono-substituted allylic *o*-DPPB esters [28]. For example:



A new class of organophosphorus ligands, *o*,*o*′-dimethylene(tri-*p*-cresyl) bicyclophosphite has been studied as a promoter of $Rh(CO)_2(acac)$ in olefin hydroformylation. *o*,*o*′-Dimethylene(tri-*p*-cresyl) bicyclophosphite was found to enhance the activity and stability of the catalyst much more strongly than PPh_3, $P(OPh)_3$, and etriolphosphite [29]. An extended X-ray absorption fine structure characterization of dilute rhodium-PEt_3 catalysts of the 1-octene hydroformylation reaction was made in supercritical carbon dioxide [30]. The effect of bite angle on 1-dodecene hydroformylation catalyzed by various diphosphine–rhodium complexes were studied [31].

A rhodium catalyst modified with tetrakis-(2,4-di-*t*-butylphenyl)-4,4′-biphenylphos phonite was found to exhibit excellent catalytic activity as well as stability for the hydroformylation of mixed olefins, especially butane dimer [32].

A new class of phospabarrelene (**6**)-rhodium catalysts has been described which allow the hydroformylation of internal alkenes with very high activity and no alkene isomerization [33].



(R = Ph, ^{i}Pr, 2,4-Xylyl)

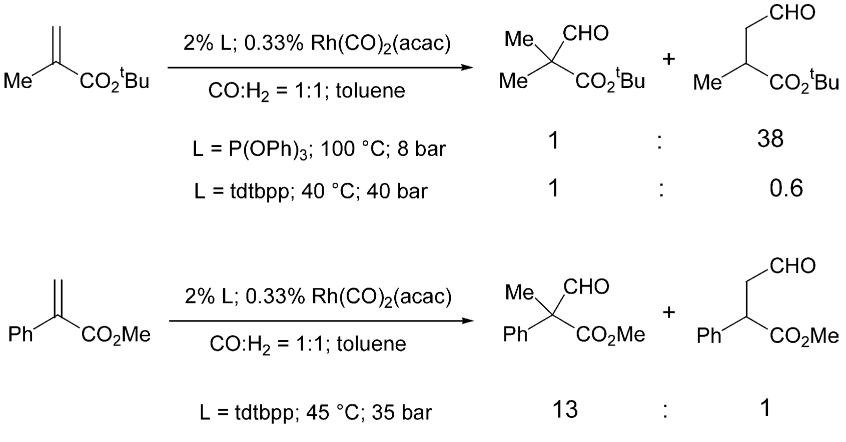
6

Rhodium complexes with the formula [RhBp(CO)P] (Bp = bis(pyrazolylborate), P = $P(NC_4H_4)_3$, PPh_3, P(*p*-MeO-$C_6H_4)_3$) were tested as catalyst precursors in the hydroformylation of 1-hexene. Yields of aldehydes of 80–87% were obtained at 80 °C and 10 bar $CO:H_2$ = 1:1 without extra phosphane as co-catalyst [34].

The rhodium(I) complex $(tpms)Rh(CO)_2$ (tpms = tris(pyrazoyl)methanesulfonate) was found to catalyze the hydroformylation of 1-hexene, reaching an activity maximum at about 60 °C. When the hydroformylation was performed in acetone, all of the rhodium was recovered at the end of the reaction in the form of the rhodium(III) bis(acyl complex $(tpms)Rh(COC_6H_{13})_2$ [35].

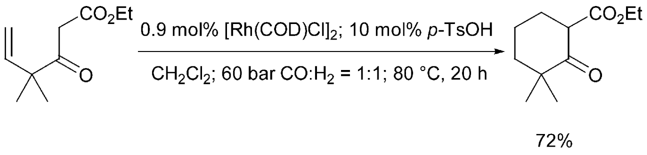
The kinetics of the $HRh(CO)(PPh_3)_3$-catalyzed hydroformylation of high-molecular-weight *cis*-1,4-polybutadiene in monochlorobenzene solution were studied. The hydroformylation reaction was found to be first order with respect to the catalyst and carbon–carbon double bond concentrations and $CO:H_2$ = 1:1 pressure. The apparent activation energy for the hydroformylation of *cis*-1,4-polybutadiene over a temperature range of 60–80 °C was estimated to be 41 kJ/mol [36].

Various phosphane-modified rhodium catalysts were tested for the hydroformylation of unsaturated esters. Pronounced temperature dependence was observed on the regioselectivity and catalytic activity for these reactions. Under appropriate conditions, either linear or quaternary products could be preferentially obtained [37]. For example:

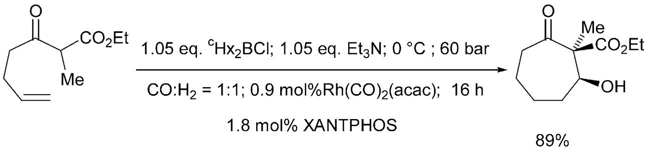


tdtbpp = (2,4-di-^{t}Bu-$C_6H_3O)_3P$

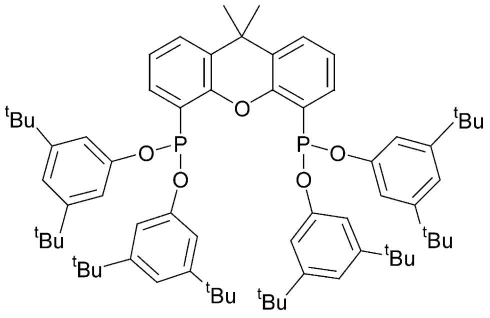
The one-pot hydroformylation/aldol reaction sequence was applied to unsaturated ketones and ketoesters in the presence of a rhodium catalyst to afford the corresponding carbocyclic aldol adducts in good yields [38]. For example:



The rhodium-catalyzed one-pot enolboration/hydroformylation/aldol addition sequence was used for the regio- and diastereoselective formation of carbocyclic quaternary centers from acyclic olefins [39]. For example:



Sterically constrained diphosphonite ligands were used for the rhodium-catalyzed hydroformylation of 1-octene and 2-butene. High activities were obtained for 1-octene, with good selectivity to the linear aldehyde. For the isomerizing hydroformylation of 2-butene using the ligand **7**, *n*-pentanal was obtained in selectivities of up to 62% [40].



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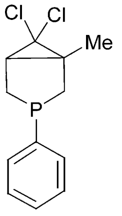
Highly active and selective catalysts for the rhodium-catalyzed hydroformylation of 1-octene and *trans*-2-octene to nonanal, and for the hydroformylation of 2-pentene to hexanal were obtained by employing phenoxaphosphano-modified XANTPHOS-type ligands [41].

The effects of pressure from 70 to 5500 bar on the phosphine-modified rhodium-catalyzed hydroformylation of linear olefins were investigated. At high pressures, the yields of aldehydes increased. Lower linear:branched ratios at higher pressure were believed to result from the formation of an unmodified rhodium catalyst. At high-pressures, increased yields of aldehydes were obtained from the hydroformylation of sterically hindered olefins [42].

The kinetics and mechanism of the hydroformylation of styrene catalyzed by the rhodium-1,2,5-triphenyl-1*H*-phosphole system were studied [43]. The kinetics of the isomerizing hydroformylation of *trans*-4-octene in toluene and in propylene carbonate catalyzed by the $Rh(CO)_2$ (acac)/BIPHEPHOS system were investigated. The observed kinetics in propylene carbonate were found to be practically the same to those in toluene. However, the selectivity in the target product *n*-nonanal was up to 95% in the former solvent [44].

Hydroformylation of styrene catalyzed by rhodium(III) complexes and the ethoxycarbonylation of styrene catalyzed by palladium(II) complexes containing novel phosphine ligands **8**–**14** were described. Using these ligands in $RhCl_2(Cp^*)$ (monodentate P-ligand) complexes as the catalyst precursor in styrene hydroformylation led to higher than 99% chemoselectivity. A strong dependence of the regioselectivity on the P-substituents was found for P-heterocyclic ligands **8**–**11** [45].



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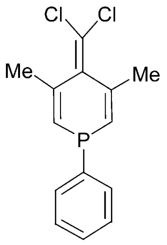

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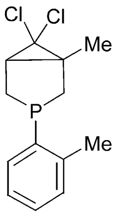

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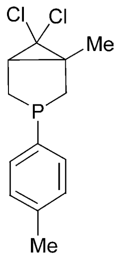

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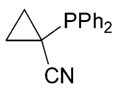

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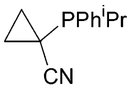

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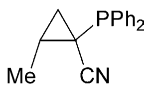

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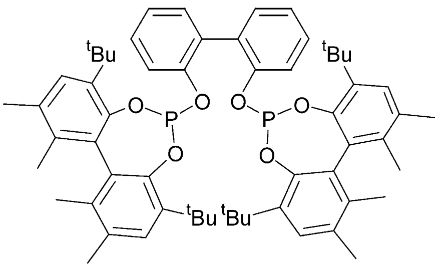
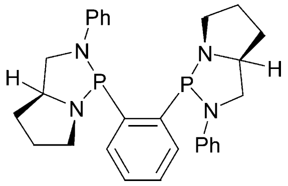
The asymmetric hydroformylation of 4-fluoro-styrene and vinyl acetate catalyzed by a diphosphite–rhodium complex was studied. High catalytic activity and good regioselectivity and up to 38% ee were observed [46].

A series of new mono- and bidentate phosphites were screened as ligands in the rhodium-catalyzed asymmetric hydroformylation of allyl cyanide. The bisphosphite **15** with a 2,2′-biphenol bridge was found to be the best overall ligand leading up to 80% ee and to a branched:linear ratio of 20 with turnover frequency of 625 h^{-1} at 35 °C [47].



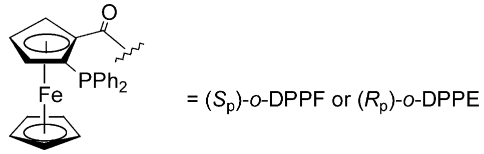
15

The optimum conditions for the asymmetric hydroformylation of vinyl acetate using the ESPHOS-ligand-modified rhodium catalyst have been elaborated (ESPHOS = **16**) [48].



16

Desymmetrizing triphenylphosphite-modified rhodium-catalyzed hydroformylation with the aid of a planar chiral catalyst-directing group (**17**) was communicated. The hydroformylation of *ortho*-diphenylphosphinylferrocene carboxylates of bisalkenylcarbinols and bisallylcarbinols was found to give enantiomerically pure *syn* aldehydes and enantiomerically pure *anti*-aldehydes, respectively [49]. For example:



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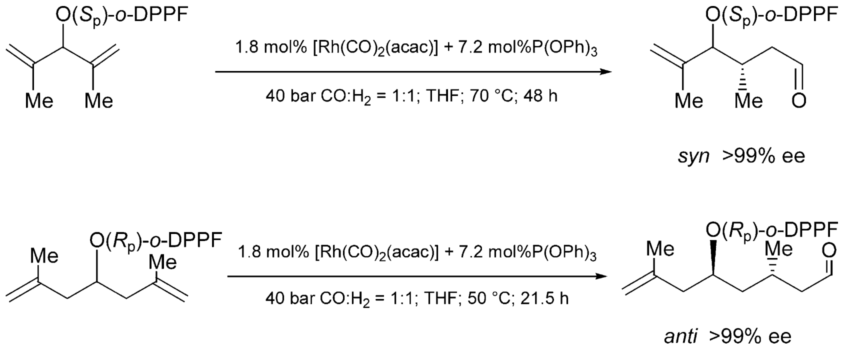
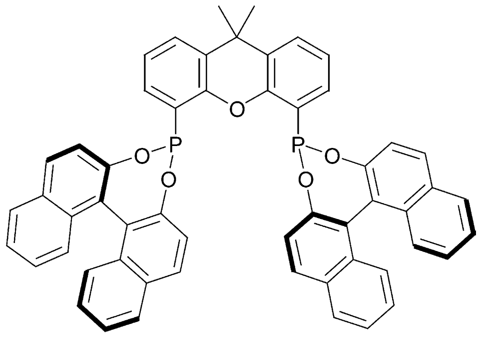


The electronic and steric effects of phosphinite ligands on activity and enantioselectivity in the rhodium diphosphinite-catalyzed asymmetric hydroformylation of styrene were investigated. In two series of ligands based on (*S*)-1,1′-bi-2-naphthol and (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphthol, the basicity was varied by using 4-CH_3, 4-CF_3, 3,5-$(CH_3)_2$, and 3,5-$(CF_3)_2$ substituents on the diphenylphosphine moieties. An increase in activity and in enantioselectivity as well as an increase in the linear:branched aldehyde ratio was observed with decreasing phosphinite basicity [50].

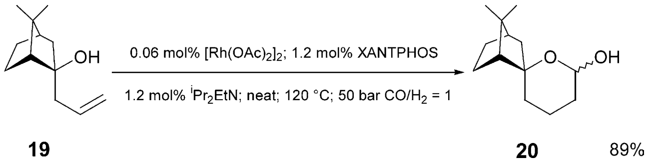
A new protocol in multisubstrate screening using an array of parallel reactors for catalyst evaluation in modified rhodium-catalyzed asymmetric hydroformylation reactions was described. The method was demonstrated using a mixture of styrene, allyl cyanide, and vinyl acetate. Among 78 catalysts based on phosphites, phosphines, and phosphoramidites the phosphite **15** was found to be the most selective ligand. Rhodium catalysts with this modifier gave 88% ee and >100:1 branched:linear regioselectivity in asymmetric hydroformylation of vinyl acetate [51].

Rhodium complexes containing chiral diphosphite ligands prepared from (1*R*,5*S*,6*R*)-(*trans*,*trans*)-spiro[4,4]nonane-1,6-diol with chlorophosphites were tested in the asymmetric hydroformylation of styrene. Moderate enantioselectivity, up to 49% ee, was obtained [52]. Low enantiomeric excesses were found in the asymmetric hydroformylation of styrene and vinyl acetate using the chiral phosphonite (**18**)-modified rhodium catalyst [53].



18

The XANTPHOS-modified rhodium-catalyzed hydroformylation was used for the preparation of **20** from **19** [54].



See also Refs. [7,58,64–66,77,85,92,136].

1.1.3. Other metals as catalysts and bimetallic catalysts

A new hydroformylation of alkenes using carbon dioxide as a reactant in the presence of a ruthenium cluster complex and halide salts was found. Similar or even better yields of alcohols were obtained as compared to the conventional hydroformylation with CO under the same reaction conditions [55].

The origin of synergism in the $Rh_4(CO)_{12}$-catalyzed hydroformylation of cyclopentene promoted with $HMn(CO)_5$ was investigated by in situ high-pressure FTIR spectroscopy. Only four organometallic species, $Rh_4(CO)_{12}$, $C_5H_9CORh(CO)_4$, $HMn(CO)_5$, and $Mn_2(CO)_{10}$, were found in the reaction mixture. The kinetics of cyclopentanecarboxaldehyde formation suggest that the origin of synergism is the $HMn(CO)_5$-attack on the acyl species [56]. The mechanism of the iridium-catalyzed hydroformylation has been studied by NMR spectroscopy. Species including iridium acyl and alkyl dihydride intermediates were detected [57].

Quantum mechanical calculations at the MP4(SDQ)//MP2 level of theory were carried out to evaluate the energies and reaction mechanisms involved in the olefin hydroformylation promoted by a homogeneous Pt-Sn catalyst. It was concluded that the hydrogenolysis and carbonylation processes are the slowest steps of the Pt-Sn-catalyzed olefin hydroformylation cycle [58].

A platinum-XANTPHOS tin(II) chloride system was found to be an active catalyst at 25–100 °C and 120 bar of $CO:H_2 = 1:1$ in the hydroformylation of styrene. High chemo- and regioelectivities of up to 99.8 and 88%, respectively, were observed [59]. Deuterioformylation of styrene using a Pt-Sn catalyst system was investigated. The results of deuterioformylation with [(2*S*,4*S*)-BDPP]Pt($SnCl_3$) as the catalyst showed that platinum hydride addition to styrene is largely irreversible at 39 °C, but reversible at 98 °C [60].

See also Refs. [82,115].

1.2. Heterogeneous systems

1.2.1. Supported metal catalysts

Mono- and bimetallic shell catalysts produced by ion beam assisted deposition were studied in hydrogenation and hydroformylation reactions. In 1-decene hydroformylation at 160 °C and 150 bar $CO:H_2 = 1:2$ using a 750 nm rhodium deposit on Al_2O_3 as the catalyst, a 62.6% yield of aldehydes was observed. Among the bimetallic catalysts the Rh-Pt catalyst showed the highest activity and the Rh-Zr catalyst the highest aldehyde selectivity [61].

The hydroformylation of ethylene and 1-hexene using PPh_3-modified highly dispersed rhodium metal catalyst on SiO_2 was investigated. At 100 °C and 10 bar $CO + H_2$ pressure the activity of the PPh_3-modified catalyst in the hydroformylation reaction was found to be higher than that of Rh/SiO_2 [62,63].

The effect of temperature, pressure, and solvent on the yield of oxygenates in the low-pressure hydroformylation of 1-hexene over active carbon and silica-supported noble metal (Ru, Rh, Pd, and Pt) catalysts were studied [66].

1.2.2. Supported complexes

The catalytic activity of rhodium complexes supported on $Al_2O_3–ZrO_2$ in hydroformylation was tested. Tethered $Rh(CO)_2{}^+$ species were found to be active for olefin isomerization but poor catalysts for hydroformylation of 1-hexene at 80 °C and 10 bar $CO:H_2 = 1:1$ [65].

SiO_2-tethered rhodium complexes derived from $Rh(CO)_2$-(acac) and 3-(mercapto)propyl- and 3-(1-thioureido)propyl-functionalized silica gel, respectively, were used as catalysts in the hydroformylation of various vinyl arenes and vinyl acetate. Conversions, chemo- and regioselectivities obtained with the SiO_2-tethered catalysts were comparable with those of the well-known homogeneous rhodium catalysts [66].

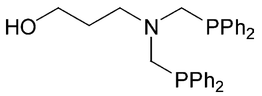
Hydroformylation of various unsaturated substrates, such as 1-octene, *trans*-2-octene, *trans*-3-octene, cyclohexene, limonene, and styrene, was carried out using as the catalyst an oligomeric complex obtained by adding $Rh(CO)_2$(acac) to oligo-1,4-phenyleneterephthalamide. Complete chemoselectivity to the oxo-products and acceptable regioselectivities were observed [67].

Catalysts obtained by immobilizing the rhodium complexes [Rh(CO)(P)(acac)] and [$Rh(P)_2$(acac)] ($P = Ph_2PCH_2CH_2Si(OMe)_3$) onto silica were tested in the hydroformylation reaction of 1-hexene. The hydroformylation activity was found to be strongly dependent on the presence and concentration of the PPh_3 co-catalyst. Without added PPh_3 both catalysts effect mainly the isomerization of 1-hexene to 2-hexene [68].

A phenoxaphosphane-modified xanthene-type compound covalently anchored on a polysiloxane support was used as a ligand in the rhodium-catalyzed hydroformylation of 1-octene in toluene and in supercritical carbon dioxide. The hydroformylation results obtained with the heterogenized ligand were found to be competitive with those obtained with homogeneous systems employing XANTPHOS as the ligand [69].

Several phosphane ligands functionalized with glycine–urea groups and bound reversibly to silica were used as a ligand system in the rhodium-catalyzed hydroformylation of 1-octene. No catalyst deterioration or metal leaching was observed in 11 consecutive reaction cycles at 80 °C and 50 bar $CO:H_2 = 1:1$ [70].

A rhodium(I) diphosphine complex, [Rh(**21**)(COD)]Cl, anchored on functionalized carbon support was tested as a catalyst for the hydroformylation of 1-octene. It was found that the catalyst shows an outstanding behavior, being fully active and with almost constant selectivity to the linear aldehyde in four consecutive catalytic runs [71].



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Rhodium complexes of (4-*tert*-butylphenyl)diphenylphosphine and bis-(4-*tert*-butylphenyl)phenylphosphine were attached to amino group functionalized mesoporous molecular sieves MCM-41 and MCM-48, and used as catalysts in the hydroformylation reaction of 1-hexene in the liquid phase. The heterogenized catalysts were found to show catalytic activity and normal heptanal selectivity comparable to the corresponding homogeneous ones [72]. The rhodium complex, $RhCl(PPh_3)_3$, chemically tethered to the surface of the mesoporous molecular sieve MCM-41 through $(EtO)_3Si(CH_2)_3NH_2$, was studied as a catalyst in the hydroformylation of cyclohexene. High activity and fair stability of the catalyst was observed at 100 °C and 28 bar $CO:H_2 = 1:1$ [73–75]. Similar results were obtained with catalysts prepared from $[RhCl(CO)_2]_2$ [76].

Comparative catalytic studies were performed of the aminated MCM-41-tethered rhodium complexes and the corresponding untethered rhodium complexes in 1-hexene [77], 1-octene, and styrene [78] hydroformylation at 80 °C and 2–20 bar $CO:H_2 = 1:1$. The influence of added PPh_3 on the catalytic activity and the *n*/*iso* aldehyde ratio was also investigated [77,78].

1.2.3. Biphasic systems

An improved hydroformylation of 1-hexene with CO_2 as the carbonyl carbon source using $Ru_3(CO)_{12}$ as the catalyst precursor in a biphasic system consisting of ionic liquid and organic solvent has been reported. In the presence of 2 mol% $Ru_3(CO)_{12}$ 1-hexene gave in a toluene/[bmim]Cl system at 140 °C and 80 bar $CO_2:H_2 = 1:1$ in 30 h an 84% total yield of C7 alcohols [79].

The water-soluble ruthenium complex, $RuH_2(CO)(TPPMS)_3$ (TPPMS = $Ph_2P(4\text{-}C_6H_4SO_3Na)$), was used as a catalyst precursor for the aqueous–biphasic catalytic hydroformylation of alkenes and alkene mixtures under mild reaction conditions. The activity trend was found to be 1-hexene > cyclohexene > 2,3-dimethyl-1-butene. The catalyst was found to be resistant to possible sulfur poisons [80].

Hydroformylation of 1-hexene catalyzed by water-soluble $CoCl_2(TPPTS)_2$ in aqueous biphasic medium was studied. At 100 °C and 90 bar $CO:H_2 = 1:1$ pressure >90% conversion with 68% selectivity for aldehyde and *n*/*iso* ratio of 3.0 for the aldehyde was found [81].

Hydroformylation of 1-octene under aqueous two-phase conditions was studied using an *N*-heterocyclic carbene rhodium catalyst immobilized to an amphiphilic, water-soluble block copolymer support. The catalyst showed high activity up to 2360 h^{-1} turnover frequency at 100 °C and 50 bar $CO:H_2 = 1:1$ pressure in four consecutive cycles [82].

The effects of methylated cyclodextrins on the $RhH(CO)(TPPTS)_3$ complex in hydroformylation conditions (50 bar $CO:H_2 = 1:1$ and 80 °C) were investigated by high-pressure ^{31}P NMR spectroscopy. It was found that the TPPTS dissociation equilibrium is influenced by the stable inclusion complex formation between methylated β-cyclodextrin and TPPTS. The methylated α-cyclodextrin does not interact with the TPPTS and the methylated γ-cyclodextrin can only weakly bind to the TPPTS. These results explain why a decrease in the normal to branched aldehydes ratio is always observed when cyclodextrins are used as mass-transfer agents in aqueous biphasic hydroformylation processes [83].

The rhodium-catalyzed hydroformylation of myrcene, limonene, and camphene was achieved in a toluene/water biphasic system employing TPPTS and cetyltrimethylammonium chloride [84]. The effect of surfactants on the activity and regioselectivity of rhodium–TPPTS-catalyzed aqueous two-phase hydroformylation of 1-hexene [85,86] and 1-dodecene [87–90] was studied.

Micelle effect of disulfonated cetyldiphenylphosphane in biphasic hydroformylation of higher olefins was investigated. Addition of $n\text{-}C_{16}H_{33}P(3\text{-}C_6H_4SO_3Na)_2$ to TPPTS–rhodium or TPPDS–rhodium hydroformylation catalysts proved to be beneficial both for the reaction rate and linear aldehyde selectivity [91].

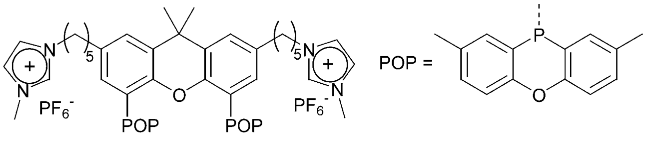
The complexes $RhH(CO)L_3$, where L = PPh_3, TPPTS, and TPPMS, were used as catalyst precursors for a comparative study of the catalytic hydroformylation of several C6 alkenes and alkene mixtures under moderate conditions in homogeneous (PPh_3) and aqueous–biphasic (TPPTS, TPPMS) media. The biphasic systems were found to be efficient for the hydroformylation of 1-hexene, 2,3-dimethyl-1-butene, styrene, cyclohexene, and mixtures thereof, in water/*n*-heptane at 80 °C [92].

The water-soluble rhodium complex Rh(μ-pz)(CO)-$(TPPMS)_2$ (pz = pyrazolate) was found to be active in the catalytic hydroformylation of 1-hexene and styrene in a two-phase reaction medium [93].

The effect of electronic and steric factors of the phosphine ligands in hydroformylation of 1-dodecene in biphasic rhodium catalytic systems was investigated using the water-soluble ligands, tris[4-methoxy-3-(sodium sulfonato)phenyl]phosphine and tris[2-methoxy-3-(sodium sulfonato)phenyl]phosphine in comparison to TPPTS [94].

Hydroformylation of 1-dodecene under aqueous–organic two-phase reaction conditions with rhodium catalysts derived from sodium salt of sulfonated 2,2′-bis(diphenylphosphinomethyl)-1,1′-biphenyl in the presence of cationic surfactants was studied [95].

A highly active and regioselective catalyst obtained from a novel dicationic phenoxaphosphino-modified XANTPHOS-type ligand **22** and $Rh(CO)_2(acac)$ for hydroformylation of 1-hexene and 1-octene in 1-butyl-3-methylimidazolium hexafluorophosphate was reported. At 100 °C high turnover frequencies (>6200 h^{-1}), high linear:branched ratios (>40) and negligible catalyst loss (Rh-loss < 0.07%, P-loss < 0.4%) were observed [96].



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Hydroformylation of 1-hexene in a liquid–liquid biphase reaction environment using different ionic liquids and a rhodium/tri(3-sulfonyl)-triphenyl-phosphane-1,2-dimethyl-3-butyl-imidazolium salt system as the catalyst was studied. The activity of the biphasic ionic liquid system was found to be approximately one order of magnitude lower than that observed for the conventional rhodium/PPh_3 catalyst in toluene [97]. Hydroformylation of 1-butene was studied in [bmim]BF_4/H_2O using $RhCl_3$/TPPTS as the catalyst precursor. High selectivity for the linear aldehyde product (*n*/*iso* ratio up to 9.1) was observed [98].

Ammonium salts with a polyether-tail as ionic liquids have been used in the two-phase rhodium-catalyzed hydroformylation of 1-tetradecene [99].

The rhodium(I)-catalyzed biphasic hydroformylation of 1-octene in various ionic liquids as the solvent and diphenylphosphino-*N*-methylpyridinium-bis(trifluoromethanesulfonyl)amide as ligand was investigated [100].

Rhodium complexes with the fluorous phosphine ligand $P(4\text{-}C_7F_{15}CH_2O\text{-}C_6H_4)_3$ were found to be active catalysts in the hydroformylation reaction of 1-octene in biphasic fluorous system (TOF = 380 h^{-1} at 80 °C and 40 bar $CO:H_2 = 1:1$) [101].

A novel continuous homogeneous catalytic system for the long-term testing of hydroformylation in fluorous biphasic systems was developed. Conversion levels up to 70% were observed, with linear to branched product ratios of around 12 [102].

See also Refs. [25,105].

1.3. Coordination chemistry related to hydroformylation

The band-target entropy minimization was applied in the IR spectroscopic investigation to detect new complexes in the $Rh_4(CO)_{12}$-catalyzed homogeneous hydroformylation of ethylene. The spectrum of $EtC(=O)Rh(CO)_3(C_2H_4)$ was identified [103].

The origin of chemoselectivity in the hydroformylation of alkenes catalyzed by trialkylphosphane complexes of rhodium was investigated. In alkene hydroformylation reactions carried out in protic solvents, monophosphane acyl intermediates were found to be responsible for the aldehyde formation in the case of P^iPr_3 and P^iBu_3, while a disubstituted acyl intermediate was found to be responsible for the alcohol formation in the case of PEt_3 [104].

See also Ref. [40].

1.4. Engineering aspects of hydroformylation

The mass-transfer effects in the biphasic hydroformylation of propene were studied using a water-soluble rhodium catalyst. It was shown that the accurate knowledge of the mass-transfer parameters in the gas–liquid system is necessary to predict and to optimize the production rate of *n*-butyraldehyde [105].

The phase-transfer and distribution of 1-octene in fluorous biphasic hydroformylation was studied [106]. The design of a continuous reactor for fluorous biphasic reactions under pressure and its use in $RhH(CO)_3[P(4\text{-}C_6H_4C_6F_{13})_3]$-catalyzed 1-octene hydroformylation was reported [107].

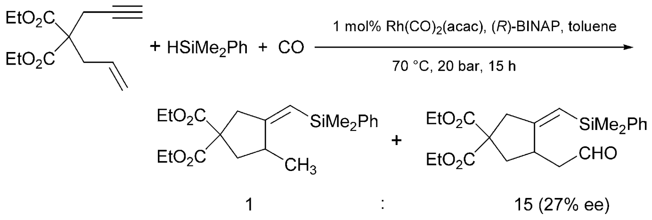
Determination of carbon monoxide solubility in ionic liquids and the relevance to the $RhH(CO)(PPh_3)_3$-catalyzed hydroformylation was communicated [108]. The continuous flow hydroformylation of 1-octene catalyzed by Rh/[Rmim][$Ph_2PC_6H_4SO_3$] (Rmim = 1-propyl-, or 1-pentyl-, or 1-octyl-3-methylimidazolium) using supercritical carbon dioxide as a transport vector was studied [109].

2. Hydroformylation related reactions of CO

2.1. Silylformylation and silylcarbocyclization

Cationic carboxylato dirhodium(II) complexes with oxo thioether ligands were found to be promising catalysts of the silylformylation reaction of 1-hexyne with dimethylphenylsilane [110].

Rhodium-, cobalt-, or iridium-promoted cyclization of 1,6-enynes in the presence of a hydrosilane and carbon monoxide was found to lead to the selective formation of functionalized cyclic compounds. Using chiral phosphine-type ligands give enantiomerically enriched carbocycles with modest enantioselectivities [111]. For example:



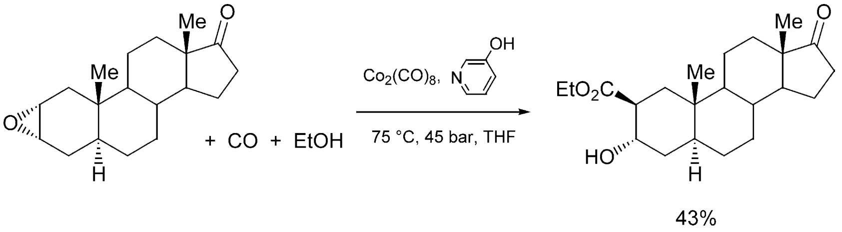
Reaction of 1,6-enynes with hydrosilane in the presence of immobilized cobalt/rhodium bimetallic nanoparticles was found to give 2-methyl-1-silylmethylidene-2-cyclopentanes in the absence of carbon monoxide and 2-formylmethyl-1-silylmethylidene-2-cyclopentanes under 1 bar carbon monoxide, respectively [112].

2.2. Hydroxycarbonylation, hydroalkoxycarbonylation, and alkoxycarbonylation

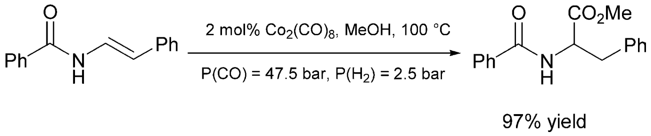
The ruthenium(II) complex *fac*-$[Ru(CO)_2(H_2O)_3C(=O)\text{-}C_2H_5)][CF_3SO_3]$ dissolved in aqueous tetrabutylammonium hydrogensulfate or sodium hydrogensulfate was found to catalyze the hydrocarboxylation of ethylene to propionic acid under water–gas shift conditions at 150 °C and 88 bar $CO:C_2H_4 = 1:1$ [113].

5-Hexenoic acid methyl ester was hydrocarboxylated using a $Co_2(CO)_8$/γ-picoline precatalyst system at 150 °C and 200 bar CO pressure in methanol. An isolated yield of 82% of isomeric dienoic acid methyl esters ($n/i = 80/20$) was obtained [114].

Ring-opening alkoxycarbonylation of epoxy-steroids using a $Co_2(CO)_8$/3-hydroxypyridine precatalyst was reported [115]. For example:



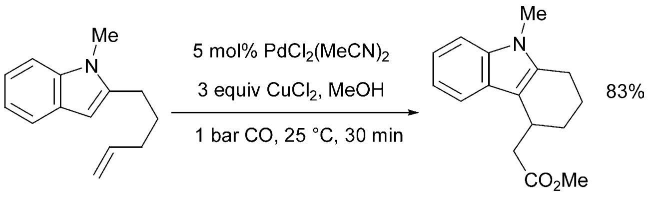
The selective hydroalkoxycarbonylation of enamides to *N*-acyl amino acid esters was reported. The use of low partial pressure in this cobalt-catalyzed hydroalkoxycarbonylation was found to be an important reaction parameter for the selective carbonylation, which prevents hydrogenation as a side reaction. A DFT calculation of the possible catalytic cycle explains the preferred pathway of this reaction [116]. For example:



In aqueous solution with tetrabutylammonium hydrogensulfate co-catalyst, rhodium complexes like *cis*-$[Rh(CO)_2(amine)_2][PF_6]$ (amine = 4-picoline, 3-picoline, 2-picoline, pyridine, or 2,6-lutidine) were found to catalyze the hydrocarboxylation of ethylene to propionic acid. An in situ FTIR spectroscopy study has confirmed that five coordinated rhodium species of the type *trans*-$[Rh(CO)_3(amine)_2]^+$ were formed under catalytic conditions at 150 °C and 88 bar CO pressure [117].

The catalytic potential of transition metal sulfides for abiotic carbon fixation was assayed. It was found that at 2000 bar and 250 °C the sulfides of iron, cobalt, nickel, and zinc promote the hydrocarboxylation reaction via carbonyl insertion at a metal sulfide-bound alkyl group. The results of the study support the hypothesis that transition metal sulfides may have provided useful catalytic functionality for geochemical carbon fixation in a prebiotic world [118].

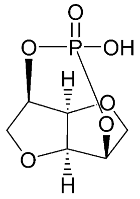
The palladium-catalyzed cyclization/carboalkoxylation of various alkenyl indoles was reported. For example, the treatment of 1-methyl-2-(4-pentenyl)indole with a catalytic amount of $PdCl_2(MeCN)_2$ and a stoichiometric amount of $CuCl_2$ in methanol under 1 bar CO at room temperature for 30 min led to the isolation of tetrahydrocarbazole **23** in 83% yield as a single regioisomer [119].



23

Hydroesterification of vinylarenes using a mixture of $PdCl_2$ and monodentate phosphorus ligands as a catalyst was studied. As ligands, methyldiphenylphosphane, neomenthyldiphenylphosphane, and dicyclohexyl(phenyl)-phosphane were found to be effective to obtain branched esters with high regioselectivity without additives such as acids. When (*S*)-2-dicyclopentylphosphino-2′-methoxy-1,1′-binaphthyl was used for the asymmetric hydroesterification of 2-methoxy-6-vinylnaphthalene, (*S*)-naproxen methyl ester was obtained with 53% ee [120].

The cyclic hydrogen phosphate **24** was used as a chiral ligand in the palladium-catalyzed asymmetric hydroxycarbonylation of styrene. Good regioselectivities (up to 97%) but low optical yields were obtained [121].



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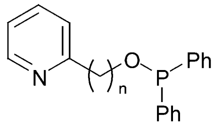
Palladium(II) complexes with 1,1′-bis(diphenylphosphino)ferrocene, 1,1′-bis(diphenylphosphino)octamethylferrocene, 1,1′-bis(diphenyphosphino)ruthenocene, and 1,1′-bis(diphenylphosphino)osmocene were used to catalyze the methoxycarbonylation of styrene. The regioselective (up to 85%) formation of 3-phenylpropanoate was observed. The highest turnover frequency (334 h^{-1} at 100 °C and 42 bar CO pressure) was obtained with the 1,1′-bis(diphenyphosphino)ruthenocene precursor in the presence of *p*-toluene sulfonic acid co-catalyst [122].

The mechanism for palladium-catalyzed alkoxycarbonylation of cinnamyl chloride was investigated. An associative mechanism was observed at low pressure, while an insertion mechanism was observed at high pressure or when an excess of ligand (PPh_3, P^cHx_3, or hemilabile P–N ligands **25**, respectively) was used [123].



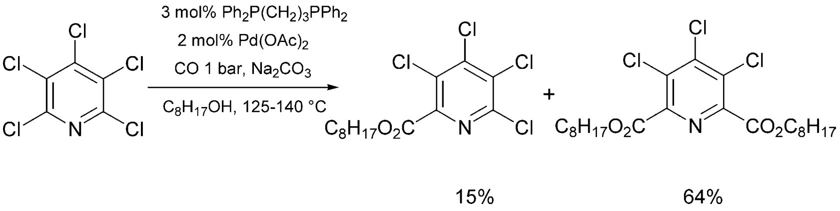
n = 1, 2, or 3

25

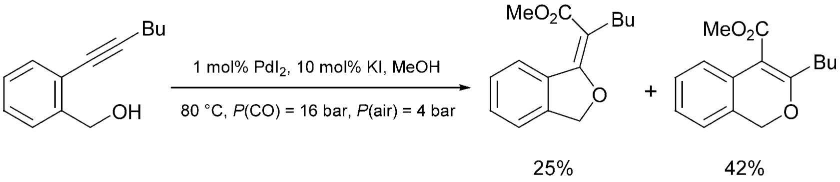
Palladium-catalyzed hydroxycarbonylation of aryl halides and benzyl chloride derivatives was studied using ionic liquid media. The use of ionic liquid media increased the yield of benzoic acid in hydroxycarbonylation of benzyl chloride [124].

The methanolysis of acyl–palladium(II) complexes relevant to palladium-catalyzed methoxycarbonylation of ethylene was found to proceed via coordination of methanol to the palladium center prior to nucleophilic attack at the acyl carbon [125].

The palladium-catalyzed carbonylation reactions of pentachloropyridine and 2,3,4,5-tetrachloropyridine were investigated. 2-Ethyl-1-hexanol was found to be an effective solvent and reactant above 100 °C and 1 bar CO [126]. For example:



The palladium-catalyzed alkoxycarbonylation reaction was used for the synthesis of 1-(alkoxycarbonyl)-methylene-1,3-dihydroisobenzofurans and 4-(alkoxycarbonyl)benzo[*c*]pyrans from 2-alkynylbenzyl alcohols, 2-alkynylbenzadehydes, and 2-alkynylphenyl ketones [127]. For example:

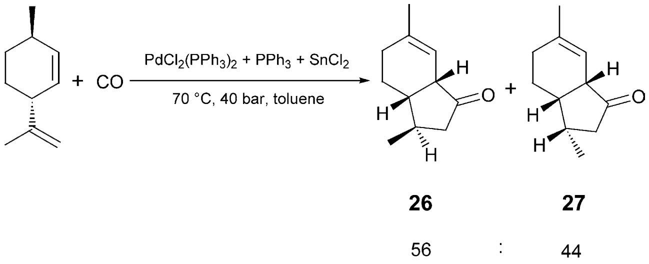


The palladium-catalyzed carbonylation reactions of haloindoles in the presence of various *N*- and *O*-nucleophiles were reported [128]. A palladium colloid prepared by reduction of the $[Pd(\eta^3\text{-allyl})_2Cl]_2$ precursor with vanadocene in the presence of polyvinylpyrrolidone as a protecting polymer was found to be an active and stable catalyst for methoxycarbonylation of iodobenzene in various ionic liquid media [129].

See also [37,45,133].

2.3. Cyclocarbonylation

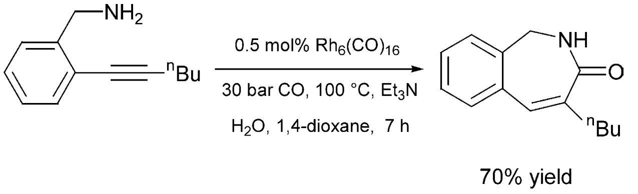
Cyclocarbonylation of (1*R*,4*R*)-isolimonene at 40 bar CO catalyzed by $[PdCl_2(PPh_3)_2]$ in the presence of $SnCl_2 \cdot 2H_2O$ and a slight excess of PPh_3, was found to give a mixture of the two cyclopentanones **26** and **27** with 84% selectivity [130].



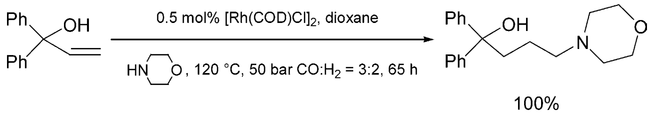
2.4. Aminocarbonylation, amidocarbonylation, and hydroaminomethylation

Density functional studies at the B3LYP/63LAN level were made on the $Co_2(CO)_8$-mediated *N*,*N*′-dimethyl-urea formation from methylamine. Two of the most probable reaction pathways for the carbonylation were proposed and examined [131]. Amidocarbonylation of alkenes with a $Co_2(CO)_8/SbR_3$ system to obtain *N*-acetyl-α-amino acids was studied [132].

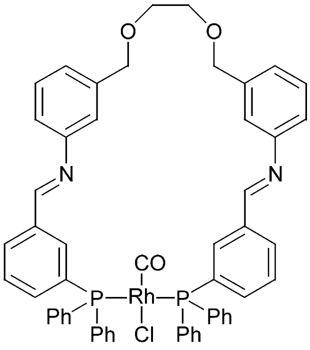
Rhodium-catalyzed carbonylation of 2-alkynylbenzylamines under water–gas shift reaction conditions was found to give a seven-membered heterocyclic product, 2,4-disubstituted-1,4-dihydrobenz[*c*]azepin-3-ones, in good yield [133]. For example:



4,4-Diarylbutylamines like Fluspirilene and 4-amino-1,1-diarylbutan-1-ols like Difenidol were prepared in high yields via rhodium-catalyzed hydroaminomethylation of 1,1-diaryl-allylalcohols. Conversion of these olefins with carbon monoxide, hydrogen and secondary amines was found to proceed with complete regioselectivity [134]. For example:



Rhodium(I) complexes with phosphine ligands bearing additional donor sites in the backbone (for example, **28**), were found to be active in the catalytic hydroaminomethylation of 1-pentene and styrene at 95 °C, $P(CO) = 5$ bar and $P(H_2) = 50$ bar [135].



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Rhodium-catalyzed tandem hydroformylation/reductive amination sequences starting from olefins were used for the synthesis of new polyamine dendrimers units in solution as well as on solid support [136].

Hydroaminomethylation of 1-dodecene with dimethylamine using a water-soluble rhodium–phosphine complex, $RhCl(CO)(TPPTS)_2$ in an aqueous–organic two-phase system in the presence of cetyltrimethylammonium bromide was investigated. High reactivity and selectivity for tertiary amine were achieved at 130 °C and 30 bar pressure [137,138].

Rhodium(I) phosphite-catalyzed hydroaminomethylation of resin-tethered amino alkenes with H_2/CO was found to give moderate to good yields of 5-, 8-, 10-, and 13-membered heterocycles [139].

Synthesis of 4-dialkylamino-5*H*-furan-2-ones from α-substituted 2-yn-1-ols, carbon monoxide, dialkylamines, and oxygen in the presence of catalytic amounts of PdI_2 was reported [140,141]. A novel polymer incarcerated palladium catalyst was found to be effective for the preparation of *N*-acyl-α-amino acids [142]. The synthesis of 1′-iodoferrocenecarboxamide or 1′-iodoferroceneglyoxylic amide by palladium-catalyzed aminocarbonylation was investigated [143].

The effect of the reaction conditions on the palladium-catalyzed aminocarbonylation of phenylacetylene in the presence of (2-pyridyl)diphenylphosphane and methanesulfonic acid was studied. The catalytic activity was found to be strongly influenced by the basicity of the amine. Good reaction rates were achieved using amines of low basicity such as aniline. The reaction solvent was found to influence both the activity and the selectivity of the catalyst. The highest reaction rates accompanied by complete regioselectivity towards the branched amide were obtained in dichloromethane/*N*-methylpyrrolidinone mixtures [144].

Various indole carboxylic acid derivatives were prepared in excellent yield by the palladium-catalyzed carbonylation of unprotected bromoindoles in the presence of different *N*- and *O*-nucleophiles [145]. The mechanism of the palladium-catalyzed amidocarbonylation was studied using phthalimide, formalhedyde, and carbon monoxide as a model system, which gives *N*-phthaloylglycine in good yield [146].

2.5. *Water–gas shift reaction and reduction with CO or $CO + H_2O$*

A novel mechanism for the gas-phase $Fe(CO)_5$ and base-catalyzed water–gas shift reaction was examined. The reaction pathway predicted at the B3LYP/6-31++G(d,p) level involves the energetically barrier less formation of $(CO)_4FeCOOH^-$, decarboxylation of $(CO)_4FeCOOH^-$ by the addition of CO to give $(CO)_4FeCHO$, and evolution of H_2 upon addition of H_2O to the $(CO)_4FeCHO$ intermediate [147].

The effects of the support (Al_2O_3, TiO_2, SiO_2, zeolite, ZrO_2, and $ZrSiO_4$) on the water–gas shift reaction activity of a ruthenium complex catalyst were investigated. The catalytic activity was found to be improved when the catalyst was supported on weakly acidic alumina [148].

Rhodium(I) complexes of the type, *cis*-$[Rh(CO)_2(amine)_2][PF_6]$ (amine = 3-picoline, 2-picoline, 2,6-lutidine, or 3,5-lutidine) in 80% aqueous amine solution were found to catalyze the selective reduction of 4-nitrobenzoic acid to 4-aminobenzoic acid at 100 °C under an atmosphere of CO [149].

2.6. *Reduction of CO_2*

The influence of the solvent and of different co-ligands on the ruthenium-catalyzed hydrosilylation of carbon dioxide was studied [150]. The ruthenium-catalyzed hydrogenation of aqueous bicarbonate was modeled [151].

The electrochemical reduction of carbon dioxide to carbon monoxide and formic acid using Co(II) hexa-azamacrocycles as an electro catalyst was studied by cyclic voltammetry and UV–vis spectroscopy [152]. The electroreduction of carbon dioxide was studied by using a glassy carbon electrode with Co(II)-tetrabenzoporphyrin as absorbed layers or as a supramolecular system. The supramolecular electrode was found to be very stable and showed a high catalytic response [153]. Co-facial dinuclear cobalt porphyrins were found to exhibit a catalytic activity for the electrochemical reduction of carbon dioxide [154].

Hydrogenation of aqueous mixtures of calcium carbonate and carbon dioxide using a water-soluble rhodium(I)-monosulfonated triphenylphosphine complex catalyst was investigated. At 50 °C and 100 bar total pressure

($P(\mathrm{CO}):P(\mathrm{H_2}) = 1:4$) the yield of formate was found to be 143% based on $CaCO_3$ [155].

3. Reviews

(1) Application of hybrid DFT/molecular mechanics to homogeneous catalysis. A review with special attention to hydroformylation by rhodium catalysts with 129 references [156].

(2) Progress in stereoselective catalysis by metal complexes with chiral ferrocenyl phosphanes. A review of recent achievements in homogeneous and single-site heterogeneous asymmetric catalysis among others in hydroformylation by metal complexes containing stereohomogeneous ferrocenyl phosphane ligands with 167 references [157].

(3) Carbohydrate derivative ligands in asymmetric catalysis. A review of carbohydrates functionalized with P, N, or S atoms and their application in transition metal-catalyzed reactions with 171 references [158].

(4) Tandem catalysis: a taxonomy and illustrative review. Tandem catalysis in organic synthesis is illustrated with examples drawn from olefin metathesis and hydroformylation chemistry with 111 references [159].

(5) New synthetic applications of tandem reactions under hydroformylation conditions. A review with 135 references [160].

(6) Multiple carbon–carbon bond formations under hydroformylation conditions. A review of transition metal-catalyzed hydroformylation sequences with various additional C–C bond-forming steps with 101 references [161].

(7) Recent advances in high-pressure infrared and NMR techniques for the determination of catalytically active species in rhodium- and cobalt-catalyzed hydroformylation reactions. A review with 174 references [162].

(8) In situ mechanistic studies in rhodium-catalyzed hydroformylation of alkenes. A review with 45 references [163].

(9) Progress in chiral ligands for asymmetric catalytic hydroformylation. A review with 72 references [164].

(10) Recent advances in rhodium-catalyzed asymmetric hydroformylation using phosphite ligands. A review covering the period from 1996 to February 2004 with 59 references [165].

(11) Chiral synthesis on catalysts immobilized in microporous and mesoporous materials. A review of recent progress on synthesis and application of chiral catalysts in porous supports among others in asymmetric hydroformylation with 159 references [166].

(12) Hydroformylation in fluorous solvents. A review of hydroformylation of long chain alkenes under fluorous biphase conditions and in neat perfluorocarbon solvents with 36 references [167].

(13) Recent advances in catalyst immobilization using supercritical carbon dioxide. A review with 39 references [168].

(14) Recent advances in the synthesis of carbonyl compounds by palladium-catalyzed carbonylation reactions of unsaturated substrates. A review with 143 references [169].

(15) Ionic liquids in catalysis. A review on the state of the art of the application of ionic liquids in catalysis with 191 references [170].

(16) Catalytic Markovnikov and anti-Markovnikov functionalizations of alkenes and alkynes: recent developments and trends with 361 references [171].

(17) Transition metal-catalyzed addition of heteroatom–hydrogen bonds to alkynes. A review with 608 references [172].

(18) Fischer–Tropsch, organometallics, and other friends. A review on the mechanism of the Fischer–Tropsch hydrogenation of carbon monoxide heterogeneously catalyzed by ruthenium, rhodium, cobalt, or iron (on silica), both with and without added probe molecules with 53 references [173].

(19) Recent advances in the homogeneous hydrogenation of carbon dioxide. A review covering advances published or in press since 1995 with 95 references [174].

Acknowledgment

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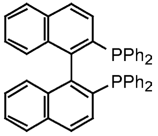
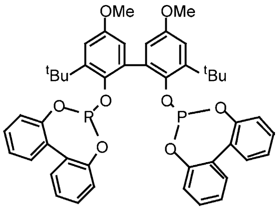
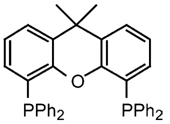
Appendix A. List of abbreviations

Ac	acetyl
acac	acetylacetonate
Ar	aryl
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl 
BIPHEPHOS	
$[\mathrm{bmim}]^+$	1-butyl-3-methylimidazolium cation
Bn	benzyl
bpy	2,2′-bipyridine
Bu	butyl

^{i}Bu	isobutyl
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
DMF	*N*,*N*-dimethylformamide
DFT	density functional theory
o-DPPB	*ortho*-diphenylphosphinylbenzoate
ee	enantiomeric excess
Et	ethyl
FTIR	Fourier transform infrared
^{c}Hx	cyclohexyl
Me	methyl
sNBD	norbornadiene
Ph	phenyl
^{i}Pr	isopropyl
py	pyridine
sc	supercritical
THF	tetrahydrofuran
TOF	turnover frequency (mol product/mol cat/time)
TPPDS	disodium salt of the disulfonated triphenylphosphine
TPPMS	sodium salt of the monosulfonated triphenylphosphine
TPPTS	trisodium salt of the trisulfonated triphenylphosphine
Ts	tosyl (*p*-toluenesulfonyl)
TsOH	*p*-toluenesulfonic acid
XANTPHOS	

Appendix B. The metals and their associated references

Metal	References
Zr	[61,65]
Mn	[56]
Re	[146]
Fe	[118,122,147]
Ru	[55,64,79,80,113,114,122,148,150,152]
Os	[122]
Co	[1–11,58,81,111,112,115,116,118,131,132,152–154]
Rh	[7,12–54,56,58,61–78,82–112,117,133,139,149,155,156,163–165,167]
Ir	[57,146]
Ni	[118]
Pd	[37,45,119–130,140–146,169]
Pt	[58–61,64,146,164]
Cu	[119]
Zn	[118]
Sn	[58–61,130]

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