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Application of transition metals in hydroformylation. Annual survey covering the year 2000

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Abstract

Hydroformylation in homogeneous and heterogeneous systems, and hydroformylation related reactions of carbon monoxide reported in 2000 are reviewed.

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

1. Hydroformylation

1.1. Homogeneous systems

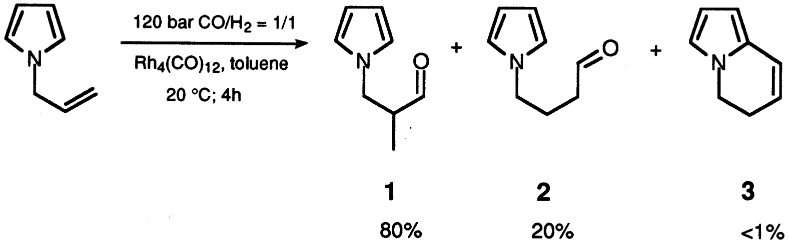
1.1.1. Cobalt catalysts

The influence of the olefin structure on the rate of hydroformylation and carbon–carbon double bond hydrogenation in the presence of $Co_2(CO)_8$ as the catalyst precursor has been studied. The ratio of the rates of hydroformylation and hydrogenation was found to correlate to the polar and steric effects of substituents in olefin molecules. The rate of the competing hydrogenation of the carbon–carbon double bond and the yield of alkanes were found to increase in the order 1-hexene < propene dimers < propene trimers < propene tetramers [1].

Hydroformylation of epoxides (ethylene oxide, propylene oxide, *trans*-2,3-butene oxide, cyclohexene oxide, and styrene oxide) in the presence of cobalt carbonyl complexes with hemilabile P–O chelating ligands ($Ph_2(CH_2)_nP(=O)Ph_2$, $n = 1, 2, 3$) was found to give β-hydroxy-aldehydes in high selectivities and yields. The best result in ethylene oxide hydroformylation, 90% selectivity toward 3-hydroxypropanal, was observed at 100°C and 100 bar of $CO:H_2 = 1:1$ using $Ph_2PCH_2P(=O)Ph_2$ in a 1:1 ligand:Co molar ratio [2].

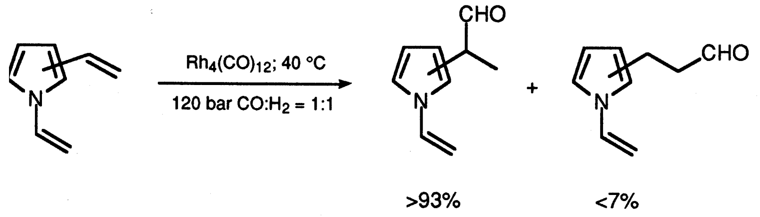
1.1.2. Rhodium catalysts

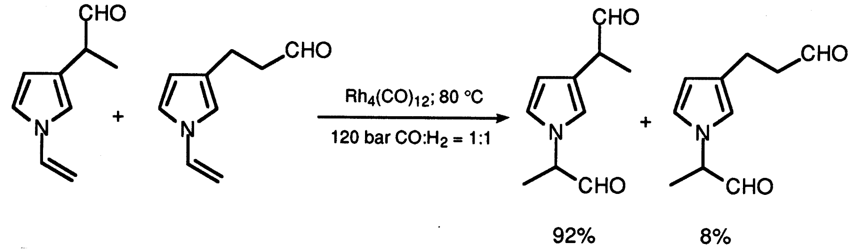
Rhodium-catalyzed hydroformylation of 1-allylpyrrole at 120 bar $CO:H_2 = 1:1$ between 20 and 100°C give as main products the branched aldehyde **1**. Using a longer reaction time the minor linear isomer **2** converts into 5,6-dihydroindolizine (**3**) [3].



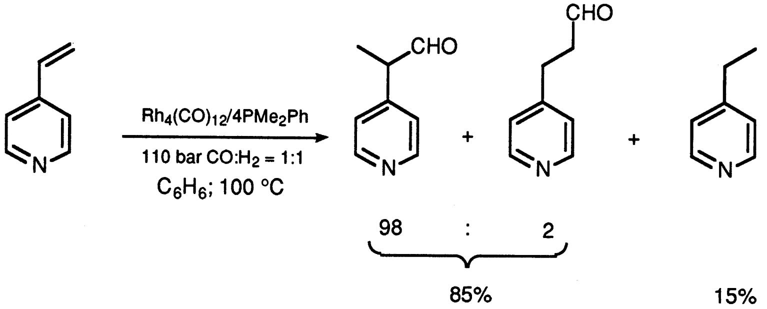
The rhodium-catalyzed carbonylation of isopropylallylamine to *N*-isopropylbutyrolactam under water–gas-shift conditions has been studied. Up to 75% of isopropylbutyrolactam formation was found at 100°C in the presence of $RhCl_3 \cdot xH_2O$ ([substrate]/[Rh] molar ratio = 200) using $CO/H_2O/THF$ at 20 bar pressure [4].

1,3-Divinylpyrrole and 1,2-divinylpyrrole were found to be hydroformylated exclusively on the ring carbon atom bonded vinyl groups at 40°C and 120 bar $H_2{:}CO = 1{:}1$ total pressure using $Rh_4(CO)_{12}$ as the catalyst precursor. The corresponding branched monoaldehydes are formed with $> 98\%$ chemoselectivity and $> 93\%$ regioselectivity. The monoaldehydes obtained from 1,3-divinylpyrrole could be hydroformylated into dialdehydes at 80°C [5].

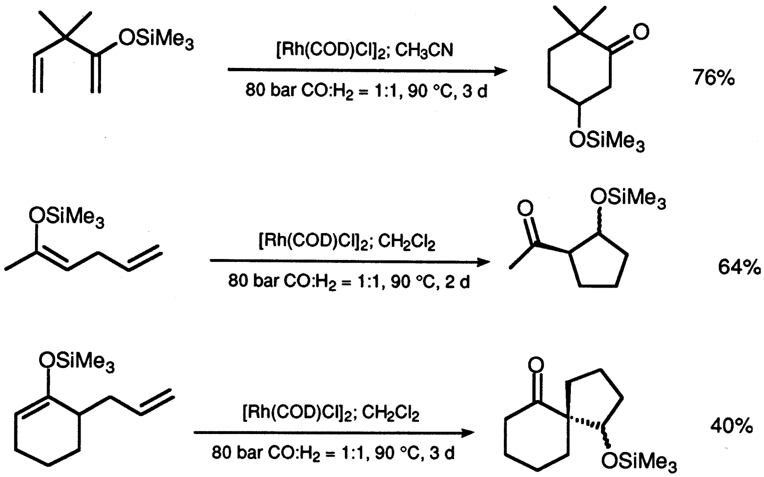




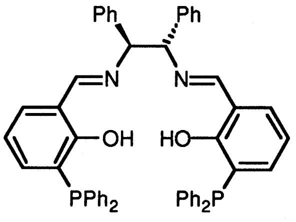
Contrary to the results obtained with the unmodified rhodium catalyst, hydroformylation of 4-vinylpyridine using a PMe_2Ph-modified $Rh_4(CO)_{12}$ catalyst gave high aldehyde selectivity and an almost complete regioselectivity into the branched isomer [6].



In a one-pot procedure β,γ- or γ,δ-unsaturated silyl enol ethers were converted to cyclic *O*-silylated aldol adducts with high selectivity and good yields through a rhodium(I) complex-catalyzed tandem hydroformylation aldol reaction [7].



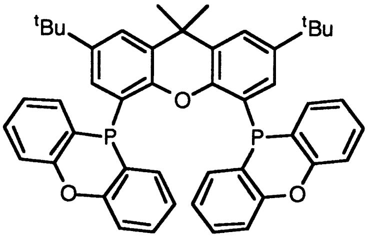
In the asymmetric hydroformylation of vinyl acetate using early-late heterobimetallic Rh–Ti complexes with chiral salenophos-type ligands, such as **4** bearing hard and soft coordination sites as the catalyst precursor, the branched aldehyde was found to be formed predominantly with up to 30% enantiomeric excess [8].



4

Catalysts derived from rhodium dicarbonyl acetylacetonate and phosphorus containing ligands were found to show high activity in hydroformylation of 2-butene, and 1-hexene but lack sufficient stability. The structure and composition of the complexes were studied using ^{31}P-NMR spectroscopy [9].

High activity and selectivity in the xantphos-type ligand-modified rhodium-catalyzed hydroformylation of 1-octene, *trans*-2- and 4-octene to linear nonanal has been observed. For example the hydroformylation of 1-octene at 80°C and 20 bar CO:H$_2$ = 1:1 using the phosphacyclic xantphos derivative **5** as the ligand of rhodium (ligand/Rh = 5, substrate/Rh = 637, [Rh] = 1.0 M in toluene) gave 88.7 ± 1.9% linear aldehyde selectivity with an extraordinary high 1557 ± 330 mol aldehyde/mol rhodium/h turnover frequency. The high activities in the case of the phosphacyclic xantphos ligand were explained by the lower phosphine basicity and the wider natural bite angles of the phosphacyclic ligands. The extraordinary high activity observed with the phenoxaphosphino-substituted xantphos ligand **5** was attributed to the four to sixfold higher rate of CO dissociation from (diphosphine)Rh$(CO)_2$H complexes compared to those with other xantphos ligands [10].



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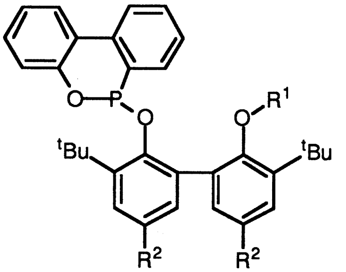
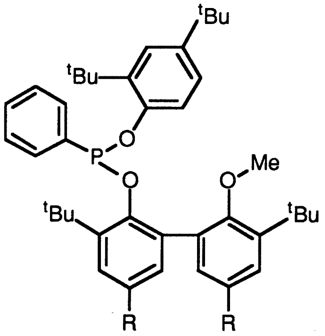
Esters of phosphonous acids **6** and **7** were found to be suitable ligands in modified rhodium-catalyzed hydroformylation of isomeric *n*-octenes. The effects of reaction variables were studied [11].

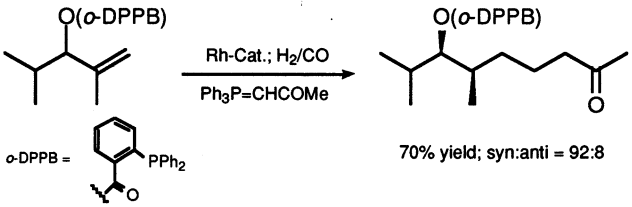


6 R^1 = Me, R^2 = OMe or ^{t}Bu
R^1 = H, R^2 = OMe



7 R = OMe or ^{t}Bu

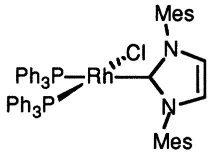
The *o*-diphenylphosphanyl benzoate-directed stereoselective rhodium-catalyzed hydroformylation of methallylic derivatives has been applied in a stereoselective domino process combining hydroformylation, Wittig olefination, and hydrogenation [12].



The *o*-diphenylphosphanyl benzoate-directed stereoselective rhodium-catalyzed hydroformylation of methallylic derivatives was applied as the starting step in a multistep synthesis to access building blocks with up to four sterogenic centers [13].

Mononuclear rhodium complexes with calix[4]arene-based monophosphites were found to be very active and chemoselective catalysts for the hydroformylation of 1-hexene but the regioselectivity is low [14]. Five different monodentate phosphites based on the calix[4]arene backbone were tested in rhodium-catalyzed hydroformylation of 1-octene. Differences in rate were correlated to the conformation of the phosphite ligand [15].

The carbene–rhodium complexes **8** and **9** were found to be active hydroformylation catalysts at 60°C and 70 bar CO:H_2 = 1:1, giving very high selectivities for the branched isomer (> 95:5) when vinyl arenes are used as substrates [16].



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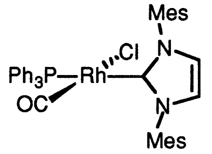
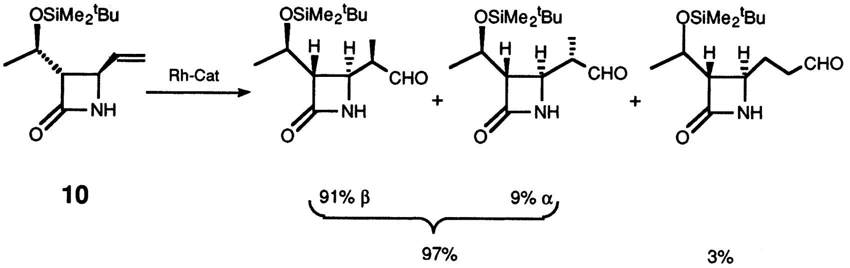


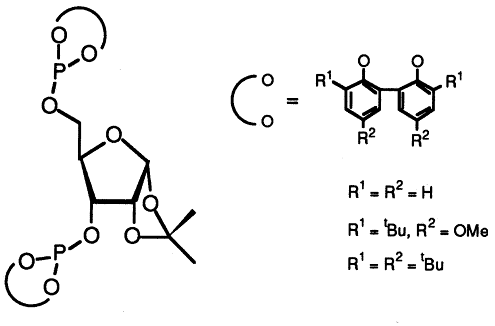
9

The asymmetric hydroformylation of a 4-vinyl-β-lactam (**10**) catalyzed by a rhodium catalyst with a chiral phosphine ligand ((NBD)$Rh^+(PhB^-Ph_3)$ + *S*,*S*-BDPP, 83 bar CO:H_2 = 1:1, 70°C, benzene) was investigated. High branched-to-linear ratio and very good stereoselectivity (β/α) was achieved [17].



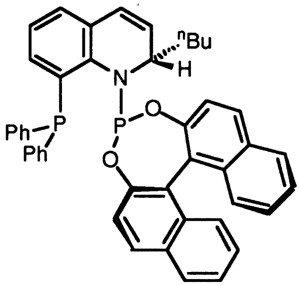
10

Ribose derivative ligands **11** have been used as catalyst components in the rhodium-catalyzed hydroformylation of styrene at 25–40°C and 25 bar CO/H_2-pressure. High (88–98%) regioselectivity for the branched aldehyde and 25–61% ee was found [18].



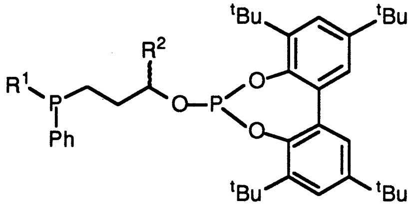
11

Chiral phosphane/phosphoramidite ligands, such as **12**, derived from quinoline were found to give up to 74% ee of (*S*)-2-phenyl-propionaldehyde in rhodium-catalyzed hydroformylation of styrene at 40°C and 100 bar $CO:H_2 = 1:1$ pressure [19].



12

The novel chiral phosphine–phosphite ligands **13** and **14** have been used in the asymmetric hydroformylation of styrene. Under mild reaction conditions ee's of 63% and regioselectivities up to 92% toward 2-phenylpropanal were obtained (25–60°C, 20 bar $CO:H_2 = 1:1$). The absolute configuration of the product was found to be governed by the stereogenic center of the backbone of the ligand [20].



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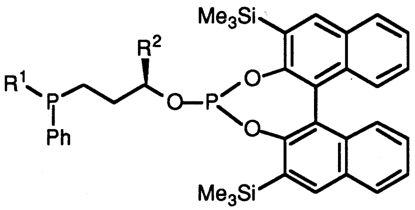
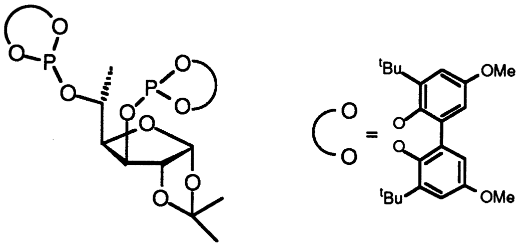


14

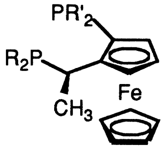
(R^1 = Ph, 2-Anisyl, 1-Napht; R^2 = Me, Ph)

Both high enantioselectivities (up to 91%) and high regioselectivities (up to 98.8%) have been achieved under mild reaction conditions (20–40°C, 10 bar $CO:H_2 = 1:1$ or 1:2) in the rhodium-catalyzed hydroformylation of vinyl arenes using a new chiral diphosphite ligand 15 derived from D-(+)-glucose [21].



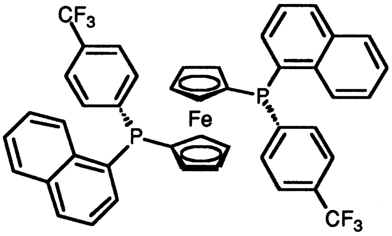
15

A variety of chiral ferrocenylethyl diphosphines **16** combined with $Rh(CO)_2(acac)$ were tested for the asymmetric hydroformylation of styrene. Some of these catalysts yield the chiral 2-phenylpropionic aldehyde with high enantioselectivity (up to 76% ee of the *S*-isomer at 40°C, 100 bar H_2:CO = 1:1, R = Ph, R′ = *o*-anisyl, $Rh(CO)_2$(acac):ligand:styrene = 1:2:300). Using a dialkylaryl–alkyldiaryl diphosphine ligand at 120°C resulted in 45% ee of the *S*-isomer [22].



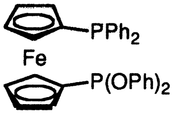
16

The effect of electronically modified derivatives of 1,1′-bis(1-naphthylphenylphosphino)ferrocene were investigated as ligands in rhodium-catalyzed asymmetric hydroformylation of styrene and substituted styrenes. In hydroformylation of styrene the best result (50% ee) was obtained at 40°C and 20 bar CO:H_2 = 1:1 by employing the ligand **17** in a ratio of 2.2:1 to rhodium [23].



17

A rhodium complex with ferrocene-based 1-phosphonite-1′-phosphine ligand 18 was tested in the hydroformylation of 1-octene and cyclohexene at 80°C and 10 bar CO:H_2 = 1:1 pressure. In the case of 1-octene all possible isomeric aldehydes (nonanal:2 - methyl - octanal:2 - ethylheptanal:2 - propylhexanal = 52:37:7:4) were formed [24].

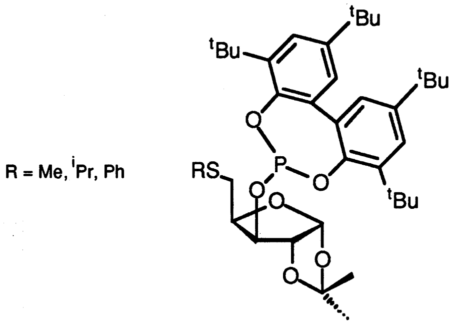


18

Rhodium complexes of the bidentate ligands 1-diphenylphosphino-1′-diphenylthiophosphinoferrocenyl and 1,2-bis(diphenylphosphino)ferrocenyl were found to be active for 1-octene hydroformylation at 80°C and 10 bar CO:H_2 = 1:1. In 1-octene methoxycarbonylation the palladium complex $Fe[C_5H_4P(S)Ph_2][C_5H_4PPh_2]PdCl_2$ in the presence of 2.5 equivalents of $SnCl_2$ per palladium gave at 95°C and 40 bar CO pressure only 8% of methyl nonanoate and methyl 2-methyloctanoate [25].

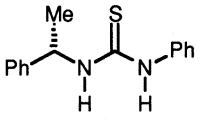
The catalytic activity in homogeneous hydrogenation and hydroformylation reactions of palladium(II) and rhodium(I) complexes, respectively, containing the bifunctional ligand $PhNHC(S)NHCH_2CH_2PPh_2$ was found to depend on the counter-anion, being very low in the case of Cl^- and high in the case of non-coordinating anionic groups such as $CoCl_4^-$ and PF_6^-. The rhodium containing xerogel using the related ligand $(EtO)_3SiCH_2CH_2CH_2NHC(S)NHCH_2CH_2PPh_2$ was found to be an active catalyst for the hydroformylation of styrene. However, metal leaching occurred to a limited extent [26]. Binuclear and polynuclear rhodium complexes containing chiral dithiolate ligands di-[(2*R*)-acetylmercaptopropyl]-phthalate and -isophthalate, in the presence of PPh_3, were tested as catalyst precursors for the asymmetric hydroformylation of styrene. Moderate activity and regioselectivity were achieved, but no enantioselective discrimination was observed [27].

Novel chiral thioether–phosphite ligands (**19**) derived from 1,2-*O*-isopropylidenexylofuranose have been tested as catalyst components in the rhodium-catalyzed asymmetric hydroformylation of styrene. Excellent conversions (> 99% in 5 h at 40°C, 25 bar $CO:H_2 = 1:1$) and good regioselectivities in 2-phenylpropanal (94%) were obtained with practically no enantiomeric excess were found [28].



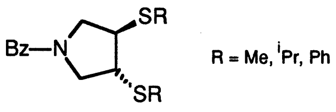
19

Chiral thioureas such as acylthiourea, dithiourea, C_2-symmetric monothiourea, and a series of disymmetric monothioureas have been examined as new chiral ligands for asymmetric hydroformylation of styrene with rhodium(I) catalysts. The best results (41% ee of (−)-2-phenyl-propanal) were obtained using **20** with $[Rh(COD)_2]BF_4$ in heptane at 40°C and 40 bar $CO:H_2 = 1:1$ (styrene:20:Rh = 350:1:1) only at low (7%) conversion [29,30].



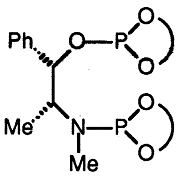
20

Cationic rhodium complexes $[Rh(COD)(L)]ClO_4$ (L = homochiral dithioethers, **21**) have been tested as catalyst precursors in asymmetric hydroformylation of styrene. The enantiomeric excess was found to be zero within experimental error. The observed regioselectivity, 46 ± 5% branched aldehyde/total aldehyde, was nearly identical to the value obtained when the catalyst precursor $[Rh_2(\mu\text{-}OMe)(COD)_2]$ was used without the dithioether ligand. It was assumed that in all cases $RhH(CO)_4$ is responsible for the hydroformylation activity [31].



21

New chiral aminophosphine phosphonite ligands with a sterogenic center of the aminophosphine phosphorus atom were applied to the rhodium-catalyzed asymmetric hydroformylation of vinyl arenes. The enantiomeric excess reached up to 77% [32]. The new ligands **22**, **23** and **24** were tested in the enantioselective rhodium-catalyzed hydroformylation of styrene. Generally, high chemoselectivities and good to high regioselectivities were found in favor of the branched aldehyde. However, the achieved enantioselectivity was low [33].



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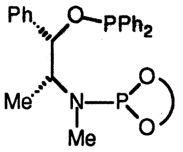

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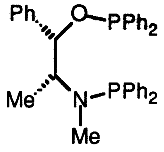

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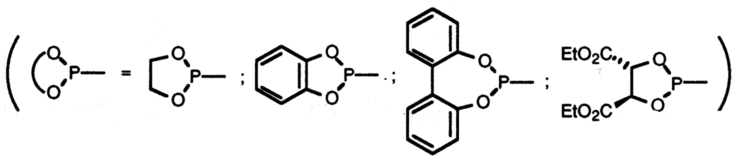
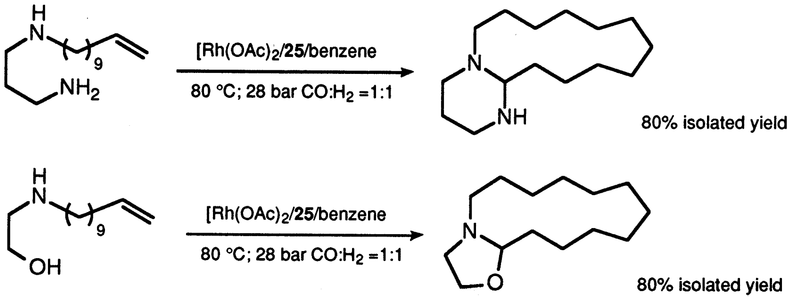


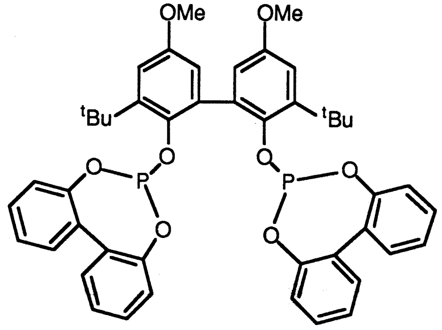
Rhodium complexes forming a nine-membered chelate ring with a chiral binaphthol based diphosphite were found to be efficient catalysts for the hydroformylation of vinylarenes at mild reaction conditions with up to 46% ee [34].

A new chiral ligand, 1,6-anhydro-2,4-bis(diphenylphosphino)pyranose was used in rhodium-catalyzed asymmetric hydroformylation of olefins. For vinyl acetate, the catalytic hydroformylation gave 96% yield of aldehydes (branched/normal = 95/5) with 92% ee of the branched isomer [35].

Diazabicycloalkanes and oxazabicycloalanes containing medium and large rings have been prepared by BIPHEPHOS(**25**)-modified rhodium-catalyzed reactions of

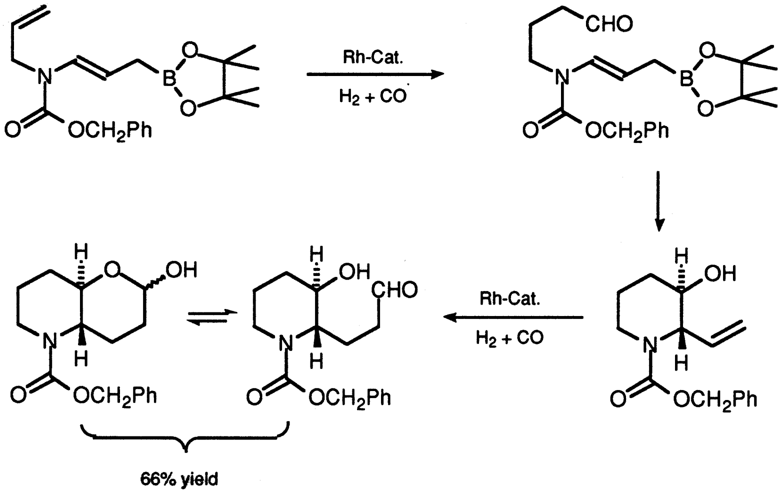
N-alkenylpropane-1,3-diamines and 2-(alkenylamino)ethanols with H_2 and CO in excellent yields without the need for high dilution [36].



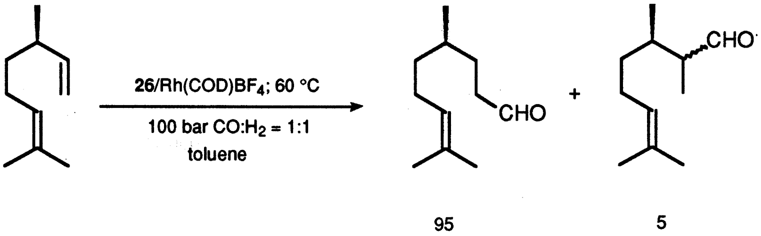


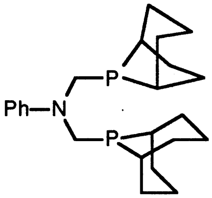
25

Hydroformylation of readily accessible allylenamides using $Rh(CO)_2(acac)$ and **25** in 1:2 molar ratio as catalyst precursor at 65°C and 5 bar of CO:H_2 = 1:1 was found to give piperidine derivatives in a domino-hydroformylation–allylboration–hydroformylation sequence [37]. E.g.:



The rhodium complex with the novel bidentate diphosphine *N*,*N*-bis-(P-(phosphobicyclo[3.3.1]nonan)methyl)aniline (**26**) ligand was found to be a highly regioselective catalyst in the hydroformylation of citronellene [38].





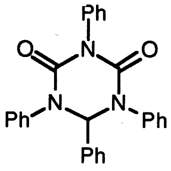
26

The rhodium-catalyzed hydroformylation of 1-octene with monodentate (**27**–**30**) and bidentate (**31**–**33**) phosphorus diamide ligands have been investigated at 80°C and 10 bar $CO:H_2 = 1:1$ pressure in toluene solution. The monodentate ligands form very active catalysts (up to 24500 mol aldehyde/mol Rh/h) but the linear to branched ratio of the product aldehydes is low ($l/b = 2.2–2.6$). The bidentate ligands show improved selectivity compared to the monodentate ligands and an activity that is only slightly lower [39].

The bis(diazaphospholidine) ligand (**34**) combined with 0.5 mol% $Rh(CO)_2(acac)$ in a $1.5 = P:Rh$ ratio was found to give an excellent catalyst for the asymmetric hydroformylation of vinyl acetate at 60°C and 8 bar $CO:H_2 = 1:1$ pressure. Thus, in 5 h 98.9% conversion, 90.3% aldehyde yield, a 94.5:5.5 = branched:linear aldehyde ratio, and a 89% ee of the (*S*)-aldehyde was achieved. Although this catalyst was active in styrene hydroformylation as well, interestingly in this case the branched aldehyde product, 2-phenylpropanal is a raceme [40].

The effects of the rhodium precursor, temperature, ligand-to-rhodium ratio, and the partial pressure of H_2 and CO in the hydroformylation of methyl methacrylate with the in situ formed (*o*-thiomethylphenyl)diphenylphosphine rhodium complex as the catalyst have been studied. The performance was compared to those with the unmodified and with the PPh_3-modified catalysts [41].

The hydroformylation of styrene using the [Rh(μ-OMe)(COD)]/BDPP catalyst precursor system was studied. Based on the kinetics and in situ high pressure infrared and NMR measurements a catalytic cycle was proposed [42].



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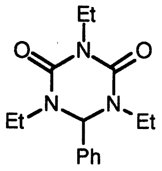

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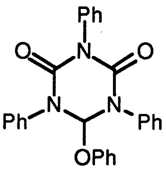

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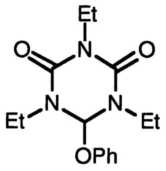

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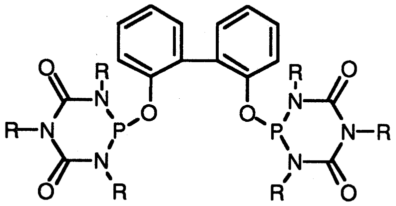

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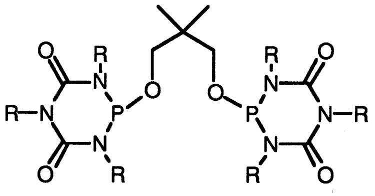
R = Ph or Et



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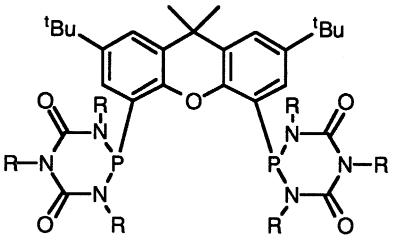

R = Ph or Et

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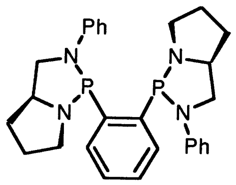

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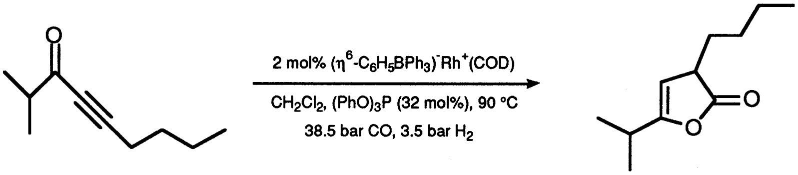
Effects of perfluoroalkyl- and alkyl-ponytails of arylphosphines on the hydroformylation of 1-decene and 1-hexadecene in supercritical CO_2 were investigated. The perfluoroalkylated ligands were found to exhibit the highest and the alkylated one the lowest activities. The high rates derived from using perfluoroalkyl-ponytails of the arylphosphines are believed to origin from the electron-withdrawing effect of their ponytails, while the slow rates observed with the other arylphosphines are believed to be mainly due to the low solubility of these ligands in supercritical carbon dioxide [43].

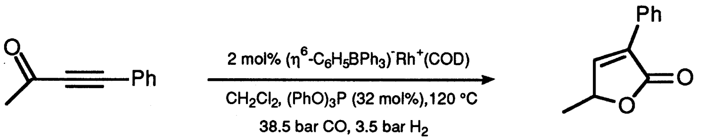
The effect of ligand modification on the activity of rhodium-catalyzed 1-octene hydroformylation in supercritical carbon dioxide has been studied at 50°C and 273 bar pressure. The activity of the rhodium catalyst formed in situ from $Rh(CO)_2(acac)$ and L (L = tertiary arylphosphine) increased with decreasing basicity of the phosphine according to the series: $P(3,5\text{-}(CF_3)_2C_6H_3)_3 > P(4\text{-}CF_3C_6H_4)_3 \approx P(3\text{-}CF_3C_6H_4)_3 > P(4\text{-}CF_3OC_6H_4)_3 > P(4\text{-}F(CF_2)_4(CH_2)_3C_6H_4)_3$. Good correlation was observed between activity and carbonyl stretching frequency for the rhodium complexes $HRh(CO)L_3$ [44].

The rhodium complex, $HRh(CO)[P(3,5\text{-}(CF_3)_2C_6H_3)_3]_3$, was found to be an extremely active catalyst in supercritical carbon dioxide for hydroformylation of 1-octene at 65°C and 273 bar total pressure with maximum turnover frequencies around 15000/h. The kinetics of the reaction was investigated. The results support the generally accepted catalytic cycle based on a dissociative mechanism [45].

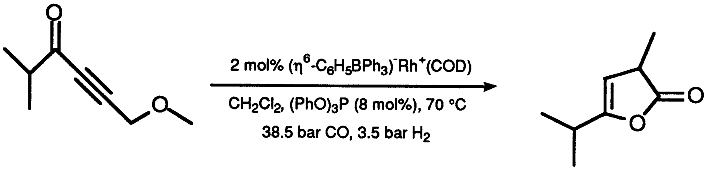
Cyclohydrocarbonylation of α-keto alkynes catalyzed by the zwitterionic rhodium complex $(\eta^6\text{-}C_6H_5BPh_3)^-Rh^+(COD)$ and triphenylphosphite was found to afford either the 2-, 2(3H)-, or 2(5H)-furanones in 61–93% yields. The cyclohydrocarbonylation is readily accomplished using substrates containing alkyl, aryl, vinyl, and alkoxy groups at the acetyleneic terminal, as well as a variety of primary, secondary, and tertiary alkyl, aryl, and heteroaryl groups connected to the ketone functionality [46]. E.g.:



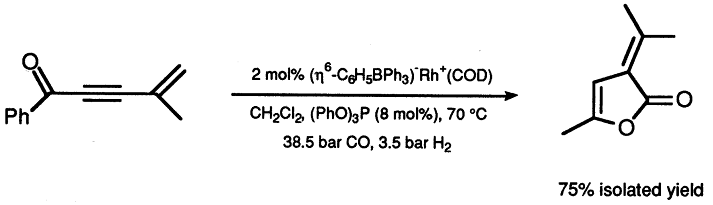
88% isolated yield



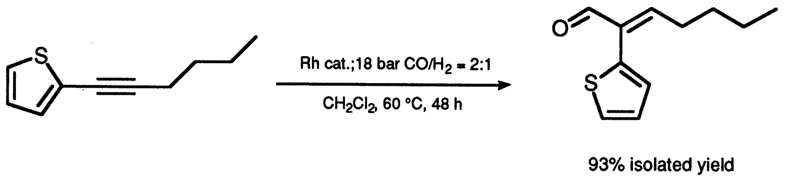
83% isolated yield



92% isolated yield



The hydroformylation of acetylenic thiophenes has been accomplished by using the zwitterionic rhodium complex $(\eta^6\text{-}C_6H_5BPh_3)^-Rh^+(COD)$ and triphenylphosphite as the precatalysts in the presence of CO and H_2 [47]. E.g.:



Rhodium catalysts with diphenylphosphine functionalized carbosilane dendrimers $Si((CH_2)_nSi(CH_3)_2(CH_2PPh_2))_4$ ($n = 2$, 3; generation 1–3) and $Si((CH_2)_nSi(CH_3)(CH_2PPh_2)_2)_4$ ($n = 2$, 3; generation 1–2) as ligands were used for 1-octene hydroformylation. The activity of the system was found to depend on the size and flexibility of the dendrimeric ligands [48]. Rhodium complexes of dendrimer phosphines with 8, 24 and 72 PR_2 arms (R = Me, Et, hexyl, cyclohexyl or Ph) based on polyhedral oligomeric silsesquioxane cores were found to catalyze hydroformylation reactions in some cases with higher linear:branched product ratio than their monomeric analogues [49].

The catalytic activity of rhodium complexes with bis(2-isopropyl-5-methylphenyl)phosphite and bis(2-*tert*-butyl-4-methylphenyl)phosphite-modified polyethylene oxide was examined in the homogeneous hydroformylation of 1-dodecene [50].

Rhodium complexes $[Rh(CO)_2L_2][PF_6]$ (L = pyridine or 4-picoline) were found to be active catalysts for the homogeneous hydroformylation of formaldehyde to give methyl formate [51].

See also Refs. [58,65,70,76,80,82–84,94–96].

1.1.3. Other metals as catalysts and bimetallic catalysts

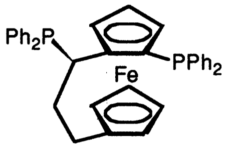
The iron complex (η^6-cyclohepta-1,3,5-triene)-(η^4-cycloocta-1,5-diene)iron was found to be an efficient catalyst precursor for the hydroformylation of 1-hexene and styrene at 100°C and 100 bar $CO{:}H_2 = 1{:}1$. Under these conditions iron pentacarbonyl as the catalyst precursor results in lower catalytic activity [52].

The heterobimetallic complex $[CH_3Zr(\mu\text{-}CpPPh_2)_2Rh(CO)PPh_3]$ (Zr–Rh) was found to be a very active catalyst for 1-hexene hydroformylation at 80°C. (Turnover frequency = 600 mol aldehyde/mol catalyst/h; $n/iso \approx 3$ with a substrate to catalyst ratio of 400.) [53].

The addition of $Fe(CO)_5$ to the systems with [Rh(acac)(CO)L] complexes (L = PPh_3, $P(OPh)_3$, $P(NC_4H_4)_3$) as catalyst precursors resulted in the increase of aldehyde yield in 1-hexene hydroformylation up to 71% at 80°C and 10 bar H_2:CO = 1:1 pressure. The formation of an unstable bimetallic intermediate, $[(H)(PPh_3)_3Rh(\mu\text{-}CO)_2Fe(CO)_4]$, was detected by infrared and ^{1}H-NMR measurements [54].

Catalyst systems consisting of a palladium(II) diphosphine complex with weakly or non-coordinating counterions were found to be excellent catalysts for the hydroformylation of both aliphatic and functionalized olefins. By variations of ligand, anion and/or solvent the catalytic reaction is directed towards alcohols, aldehydes, ketones or oligoketones. Thus, non-coordinating anions and arylphosphine ligands produce primarily (oligo)ketones; increasing ligand basicity or anion coordination strength shifts selectivity towards aldehydes and alcohols [55].

Platinum-complexes $PtCl_2(L)$ and $PtCl(SnCl_3)(L)$ (L = **35**–**37**) have been used in the hydroformylation of styrene. Below 60°C the prevailing formation of (*R*)-2-phenyl-propanal (19–38% ee), while at 100°C the formation of the (*S*)-enatiomer with up to 37% ee was observed. Palladium complexes with the ferrocenyl diphosphine ligands **32** and **36** as catalysts in hydromethoxycarbonylation of styrene proved to be rather inactive [56].



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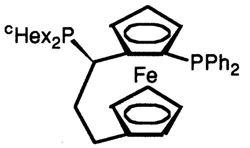

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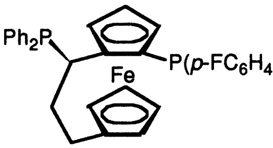

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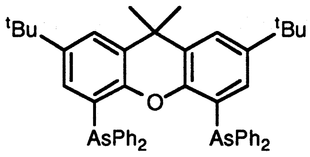
Wide bite angle arsine based ligands **38** and **39** were found to lead to very efficient platinum/tin catalysts for selective hydroformylation of terminal alkenes. The catalytic performances of the arsine-modified platinum/tin systems compete with the best results obtained using rhodium catalysts. Thus, at 60°C and 40 bar CO:H_2 = 1:1 using $[Pt(COD)Cl_2]$ as the catalyst precursor in 1-octene hydroformylation, [Pt] = 2.5 mM, Pt = $SnCl_2$:39:1-octene = 1:2:4:255, 96% nonanal was obtained with an average turnover frequency of 350 mol aldehyde/mol Pt/h at 20–30% conversion, with a linear:branched ratio of 200 [57]. The effects of various wide bite angle amine, arsine, and phosphine ligands with xanthene backbones have been studied in rhodium- and platinum/tin-catalyzed hydroformylation. An unprecedented high activity and selectivity was obtained by employing a mixed phosphine/arsine ligand **39** in the platinum/tin-catalyzed hydroformylation of 1-octene. Thus, the substitution of one diphenylphosphine group of ligand **40** for diphenylarsine increases the hydroformylation activity 20-fold at 60°C and 40 bar CO:H_2 = 1:1 pressure, without losing the excellent (~ 95%) selectivity for linear aldehyde formation [58].



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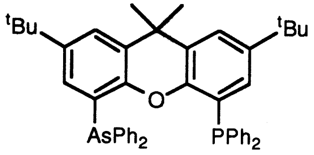

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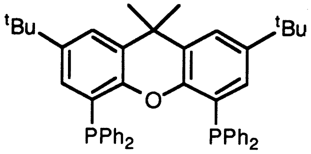

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Monoterpenes, (−)-β-pinene, (*R*)-(+)-limonene, and (−)-camphene were hydroformylated at 100°C and 90 bar CO:$H_2 = 1:1$ pressure using the catalyst system $PtCl_2(P_2)/SnCl_2/PPh_3$ (where $P_2 = (PPh_3)_2$ or the diphosphines: DPPE, DPPP, and DPPB). The effects of the catalyst composition and ligand nature on the product distribution were studied. Under optimized conditions, chemoselectivity for aldehyde formation of near 90% were observed. For all monoterpenes studied the hydroformylation gave exclusively the linear isomers of the corresponding aldehydes [59].

Platinum complexes, $PtCl_2L_2$, with L = *o*-, *m*-, and *p*-$Ph_2PC_6H_4P(=O)(OEt)_2$ combined with $SnCl_2$ were found to catalyze the hydroformylation of 1- and 2-butene at 120°C and 80 bar CO:$H_2 = 1:1$ pressure [60].

Liquid chlorostannate ionic liquid as reaction medium for hydroformylation of methyl-3-pentenoate and 1-octene at 120°C in the presence of $PtCl_2(PPh_3)_2$ as the precatalyst has been described. The platinum catalyst dissolved in chlorostannate ionic liquids shows enhanced stability and selectivity in the hydroformylation of methyl-3-pentenoate compared to the identical reaction in CH_2Cl_2. In the case of 1-octene hydroformylation, a biphasic reaction system could be realized using the chlorostannate ionic liquids as catalyst solvent [61].

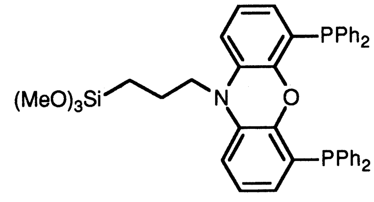
See also Refs. [8,26,107].

1.2. Heterogeneous systems

1.2.1. Supported complexes

The preparation of bimetallic rhodium–cobalt hydroformylation catalysts with rhodium loading of 1%, Rh and Co atomic ratio of 1:3 from $[Rh(CO)_2Cl]_2$ and cobalt carbonyl ($Co_2(CO)_8$ or $Co_4(CO)_{12}$) on the surface of SiO_2 has been investigated by means of in situ infrared spectroscopy. It was found that the bimetallic $RhCo_3$ cluster can be efficiently formed from $([Rh(CO)_2Cl]_2 + Co_4(CO)_{12})/SiO_2$ by thermal treatment under a reducing atmosphere [62].

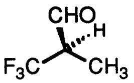
A continuous process for the selective hydroformylation of 1-octene in supercritical carbon dioxide using an immobilized rhodium–diphosphine catalyst containing a large P–Rh–P bite angle has been presented. Thus, the immobilized catalyst prepared from silica (200–500 μm), *N*-(3-trimethoxysilyl-*n*-propyl)-4,5-bis-(diphenylphosphino)phenoxazine (**41**) and Rh(acac)(CO)$_2$ converted 1-octene selectively to the linear aldehyde in a flow reactor at 80°C and 120 bar $CO_2 + 50$ bar overpressure of syngas. The average linear to branched aldehyde ratio was found to be 40:1 [63].



41

Stationary phases obtained from rhodium(I) complexes HRh(CO)[Ph$_2$P-(CH$_2$)$_{3or6}$Si(OMe)$_3$]$_3$, sol–gel processed with bifunctional cocondensation agent (MeO)$_3$SiCH$_2$Si(OMe)$_3$ and in a separate reaction also with three additional equivalents of the phosphine ligand Ph$_2$P(CH$_2$)$_{3or6}$Si(OMe)$_3$ proved to be efficient catalysts for the hydroformylation of 1-hexene in the presence of a wide variety of solvents in the interphase. Selectivities up to 92% and a *n*/*iso* ratio of 14:1 with an average turnover number of 164 mol substrate/mol catalyst/h were achieved [64].

Polystyrene-supported (*R*,*S*)-BINAPHOS–rhodium complex was applied to the solvent-free vapor-phase asymmetric hydroformylation of 3,3,3-trifluoropropene, (*Z*)-2-butene, and styrene. The aldehyde **42** is produced with 114 h^{-1} turnover frequency at 80 bar $CO:H_2 = 1:1$ and 40°C with 93% regioselectivity and 90% ee. The aldehydes **43** and **44** are produced with 27 and 157 h^{-1} turnover frequency at 32 bar $CO:H_2 = 1:1$ at 60°C with 100 and 85% regioselectivity and 80 and 91% ee, respectively [65].



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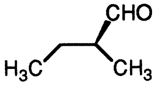

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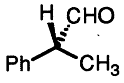


44

Several intrazeolite rhodium complexes with sulfur donor ligands were synthesized and tested in the hydroformylation reaction. These heterogenized catalysts were found to be active and selective and reusable in hydroformylation, leading to the preferential formation of the branched product [66].

Hydroformylation reactions using recyclable rhodium-complexed phosphonated polyamidoamine dendrimers on silica have been investigated. Hydroformylation of styrene and vinyl acetate was found to proceed in up to quantitative yields and good branched selectivity at 65–75°C and 70 bar $CO:H_2 = 1:1$ pressure in CH_2Cl_2. The importance of the length of the spacer chain in the dendrimer on the activity and recyclability of the dendrimer rhodium complex was demonstrated [67].

Rhodium complexes with dendritic, phosphine ligands anchored onto beads of Rink amide MBHA resin were found to be excellent catalysts for the hydroformylation of vinyl esters and styrenes. High branched/linear aldehyde product ratios were obtained ($> 10{:}1 =$ branched:linear ratio in most cases) at 65°C and 70 bar $CO{:}H_2 = 1{:}1$ pressure. The catalysts remain highly reactive even after several cycles [68].

A strategy for the immobilization of catalytically active transition metal complexes has been described in which the rhodium hydride complex $[(H)Rh(CO)(NaTPPTS)_3$ is electrostatically bound to highly charged polystyrene microspheres coated with cationic polyelectrolyte. The catalytic activity of this latex-bound catalyst in the hydroformylation of methyl acrylate at 60°C and 50 bar $CO{:}H_2 = 1{:}1$ pressure was reported and compared with its unbound equivalent [69].

See also Refs. [26,71].

1.2.2. Biphasic systems

Hydroformylation of 1-hexene and 1-nonene using insoluble rhodium catalysts in supercritical carbon dioxide has been studied. The rhodium complexes prepared in situ from $[Rh_2(OAc)_4]$ and $P(OPh)_3$, $P(OC_6H_4\text{-}4\text{-}C_9H_{19})_3$ and $Ph_2PCH_2CH(CO_2C_{16}H_{33})CH_2CO_2C_{16}H_{33}$ in supercritical carbon dioxide were found to form insoluble liquid drops in the reactor, whilst the rest of the reaction mixture is a single phase at 100°C, 40 bar $CO{:}H_2 = 1{:}1$ and 220 bar total pressure. The rhodium complexes show good catalytic activity in hydroformylation and, for the phosphites, excellent linear selectivity (up to linear:branched = 8.0) [70].

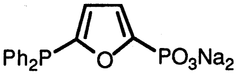
Phosphines substituted with phosphonic acid groups were used to immobilize rhodium catalysts in aqueous biphasic systems and between the layers of zirconium phosphate hybrid materials. Effective immobilization and turnover frequencies higher than 600 h^{-1} were found at 120°C and 30 bar $CO{:}H_2 = 1{:}1$ in hydroformylation of 1-octene to nonanal and 2-methyloctanal [71].

The amphiphilic ligands $Ph_2P{-}(CH_2)_{10}{-}PO_3Na_2$ and $Ph_2P{-}(CH_2)_{12}{-}PO_3Na_2$ were found to form rhodium catalysts for the aqueous two-phase hydroformylation of long-chain olefins (1-octene, 1-dodecene) which are superior to Rh/TPPTS systems. Aldehyde selectivities higher than 95% and high activities (TOF = 660/h at 88% yield) were achieved [72]. Sulfonated triphenylphosphine was tested for its activity in the hydroformylation of ethene and 1-octene in biphasic mode using $[Rh(COD)Cl]_2$ as the catalyst precursor [73]. 2,5-Dimethoxy-2,5-dihydrofuran did not give the expected aldehydes when the water-soluble rhodium catalyst (Rh/TPPTS) was used for the conversion at 70°C and under 30 bar $CO{:}H_2 = 1{:}1$ pressure. It was found that instead of hydroformylation, hydrogenation was the main reaction path in water, where 2,5-dimethoxytetrahydrofuran and its hydrolysis product, succinic dialdehyde, were obtained [74].

A protein–rhodium complex, obtained from $Rh(CO)_2(acac)$ and human serum albumin, was found to be an efficient catalyst for two-phase olefin hydroformylation (styrene, isobutene, α-methylstyrene, phenyl vinyl ether, 1-octene). In the case of styrene at 60°C and 80 bar $CO{:}H_2 = 1{:}1$ complete conversion and $> 99\%$ aldehyde yield with 95% branched product was obtained. The chemo- and regioselectivity is practically not affected in the range of 40–100°C. Hydratropaldehyde showed a low but definite enantiomeric excess of the prevailing *R*-isomer [75].

The hydroformylation of 1,1-diarylethenes, 1,1-diarylallylalcohols, and aryl vinyl ethers was studied in a biphasic system (water/toluene or water/cyclohexane) in the presence of rhodium carbonyl complexes with the water-soluble ligand sulfonated triphenylphosphine (TPPTS). The yields of the expected aldehydes were found to be generally high without any addition of co-solvents and hydrophobic auxiliary ligands. A comparison was made between reaction rate, chemo- and regioselectivity observed in the biphasic process with those obtained in the conventional oxo-reaction [76].

(2-Furyl)diphenylphosphane, bis(2-furyl)phenylphosphine, and tris(2-furyl)phosphine have been converted into their water-soluble 5-carboxylates, 5-phosphonates, and 5-sulfinates. It was found that the furan group sharply enhances the water-solubility of these products when compared with the corresponding benzene derivatives. Catalytic tests among others in rhodium-catalyzed hydroformylation of styrene showed that the sulfinate group tends to inhibit the catalysis and, in addition, a sharp drop in activity was observed with the trifunctional products. The phosphonates such as **45** were found to be the most promising ligands for biphasic catalysis. Thus, using **45** as ligand with $Rh(CO)_2(acac)$ in toluene:water = 1:1 at 65°C and 20 bar $CO:H_2 = 1:1$ gave a branched:linear aldehyde product ratio of 4.88 at 100% conversion of styrene [77].



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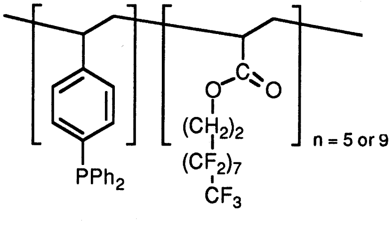
The poly(fluoroacrylate-co-styryl diphenylphosphine) ligands **46** combined with $Rh(CO)_2(acac)$, P/Rh = 6, were found to be active and selective catalysts for the fluorous biphase hydroformylation of 1-decene, 1-hexadecene, styrene, and *n*-butyl acrylate at 100 and 80°C, at 30 bar $CO:H_2 = 1:1$ pressure in hexane–toluene–perfluoromethylcyclohexane solvent mixture [78].



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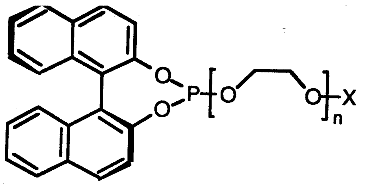
Novel water-soluble calix[4]arenes with phosphine-containing groups have been used as ligands in the rhodium-catalyzed biphasic hydroformylation of 1-octene. The catalysts function not only as metal catalysts for hydroformylation but also as inverse phase-transfer catalysts which facilitate reactions through transporting the organic substrate into the aqueous phase, leading to enhanced catalytic activity at 40 bar $CO:H_2 = 1:1$, and 100°C. Conversions of up to 98% and aldehyde yields of up to 86% with a linear/branched ratio of 1.7–3.0 was achieved [79].

Hydroformylation of 1-dodecene in an organic monophase system using a rhodium catalyst of a nonionic surface-active phosphine ligand has been studied. It was found that the $P[p\text{-}C_6H_4O(CH_2CH_2O)_nH]_3/Rh$ catalyst is insoluble in organic solvents at room temperature. At 130°C and 40 bar $CO:H_2 = 1:1$ pressure, however, a homogeneous solution is formed which converts 1-dodecene into the corresponding aldehydes. The conversion of 1-dodecene and the yield of the aldehydes are 95.8 and 93.7%, respectively. After the reaction is complete, the catalyst precipitates out from the organic solvent on cooling to room temperature, and is easily separated from the product and can be recycled efficiently [80]. The rhodium complex of nonionic surface-active phosphines, $[R(CH_2CH_2O)_n]_mPPh_{3-m}$ ($n = \, > 7$, $m = 1$ or 2, R = larger than butyl) was found to exhibit good catalytic activity in the hydroformylation of 1-dodecene in an aqueous/organic two-phase medium. High (98%) conversion of 1-dodecene and 96% yield of aldehydes was found [81]. Chiral polyether–phosphite ligands (**47**) combined with $[Rh(COD)_2]BF_4$ were found to show high activity, chemo- and regioselectivity in the catalytic enantioselective hydroformylation of styrene under thermoregulated phase-transfer conditions. Values of ee up to 25% were obtained at 40°C and 40 bar $CO:H_2 = 1:1$ pressure [82].

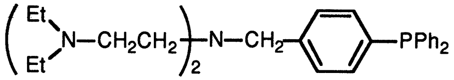


X = Me, n = 16-17
X = PO$_2$R, n = 4-5
[RO_2H_2 = (S)-Binol]

47

A highly active and selective water-soluble hydroformylation catalyst was obtained by the reaction of polyethylene glycol and rhodium trichloride hydrate. The catalyst was tested in the hydroformylation of 1-dodecene, 2,4,4-trimethyl-1-pentene and styrene. The turnover frequency for 2,4,4-trimethyl-1-pentene in the biphasic system (450 mol aldehyde/mol rhodium/h at 100°C and 100 bar pressure) was found to be three times higher than in comparable homogeneous systems [83].

The in situ generated rhodium complexes with the new amphiphilic triphenylphosphine analogue (**48**), as catalyst in the hydroformylation of 1-hexene was studied. In toluene as solvent the new catalysts exhibit features closely resembling those of triphenylphosphine complexes. Recycling of the catalyst based on the ligand **48** by extraction is possible with relatively high retention of its initial activity. The rate of hydroformylation under biphasic conditions (toluene/water) is very low, giving only about 1.4% of the turnover frequency of the same catalyst system in neat toluene [84].

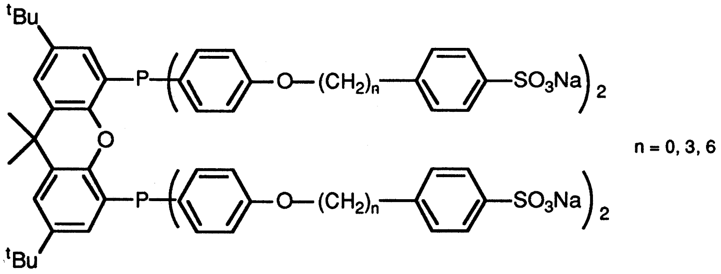


45

Rhodium(I) complexes of water-soluble dendritic phosphonated ligands with hydrophilic amine or sulfonic acid groups were used as the catalysts in the two-phase hydroformylation of styrene and 1-octene at 40–60°C and 20 bar $CO:H_2 = 1:1$ pressure. These catalysts exhibit high selectivity for the branched aromatic aldehyde (up to $i/n = 29$) and for the normal aliphatic aldehyde (up to $n/i = 4.2$), respectively [85].

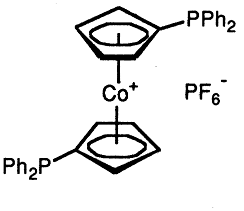
Selective rhodium-phosphine-catalyzed hydroformylation of *N*-allylacetamide in an inverted aqueous two-phase (toluene/water) catalytic system was found to provide a facile catalyst/product separation, after which the aqueous product phase containing the linear aldehyde 4-acetylamino-butyraldehyde could be used in a one-pot synthesis of *N*-acetyl-5-methoxytryptamine (melatonin) [86].

The synthesis, aggregation behavior, and biphasic hydroformylation activity of rhodium complexes of a series of xantphos derivatives with surface-active pendant groups, $-4\text{-}C_6H_4O(CH_2)_nC_6H_4SO_3Na$ ($n = 0, 3, 6$) (**49**) has been described. In the case of $n = 3$ and 6 the hydrophobic part of the ligand was found to be large enough to form stable aggregates at 90°C, and their presence lends to a significant enhancement of the solubility of organic substrates in aqueous solution. This enhanced solubility results in a higher reaction rate in the rhodium-catalyzed hydroformylation of 1-octene [87].



49

1,1′-bis(Diphenylphosphino)cobaltocenium hexafluorophosphate (**50**) was found to be a very suitable ligand for the rhodium-catalyzed biphasic hydroformylation of 1-octene in 1-butyl-3-methyl-imidazolium hexafluorophosphate. High catalyst activity (TOF = 810/h at 100°C and 10 bar $CO:H_2 = 1:1$), high selectivity to the *n*-product (*n*/*iso* = 16.2), and no catalyst leaching was observed [88].



50

See also Refs. [61,69].

1.3. Coordination chemistry related to hydroformylation

An ab initio method under the effective core potential approximation was employed to study the reaction mechanism of carbonyl insertion of the cycle of $HCo(CO)_3$-catalyzed ethene hydroformylation at the Hartree–Fock level. The structures of the $EtCo(CO)_4$ reactant, transition state of the ethyl migration reaction, and product for the reaction were determined. The energy of each stationary point was corrected at MP2/LAN2DZ/LANL2DZ + zero-point energy level. The calculated activation barrier for the ethyl migration reaction was found to be 28.89 kJ mol^{-1} [89]. A comparison of the calculated potential energy barrier for the carbonyl migration and the ethyl group migration using an ab initio method at HF/LANL2D2 level has shown that the carbonyl insertion reaction path via the ethyl migration is much more energetically favorable than that via the carbonyl migration [90].

A time-resolved infrared spectroscopic study of reactive acyl intermediates relevant to the phosphine-modified cobalt-catalyzed carbonylations has been made. Step-scan FTIR and variable single-frequency time-resolved infrared detection on the microsecond time scale were used to record the spectrum of $CH_3C(O)Co(CO)_2PPh_3$ and to demonstrate that the principal photoproduct of the subsequent reaction of this complex under 1 bar CO is the methylcobalt complex $CH_3Co(CO)_3PPh_3$. At higher pressure of CO the trapping of $CH_3C(O)Co(CO)_2PPh_3$ with CO to reform $CH_3C(O)Co(CO)_3PPh_3$ was shown to become competitive with the rate of acetyl-to-cobalt methyl migration to give $CH_3Co(CO)_3PPh_3$. Activation parameters for the competing pathways in benzene were determined to be $\Delta H^{\ddagger}_{CO} = 5.7 \pm 0.4$ kJ mol^{-1}, $\Delta S^{\ddagger}_{CO} = -91 \pm 12$ J mol^{-1} K^{-1} and $\Delta H^{\ddagger}_{CH3} = 40 \pm 2$ kJ mol^{-1}, $\Delta S^{\ddagger}_{CH3} = -19 \pm 5$ J mol^{-1} K^{-1}. The effects of varying the solvent on the competitive reactions of $CH_3C(O)Co(CO)_2PPh_3$ were also explored, and the mechanistic implications of these results were discussed [91].

The rhodium carbonyl complexes in the unmodified rhodium-catalyzed hydroformylation of conjugated diolefins were investigated by in situ high-pressure infrared spectroscopy. The presence of η^3-allyl rhodium tricarbonyl, η^1-allyl rhodium tetracarbonyl and acylrhodium tetracarbonyl species were tentatively assigned based upon the spectra [92]. The unmodified rhodium-catalyzed hydroformylation of ethene was investigated by in-situ high-pressure infrared spectroscopy. At high CO partial pressure (40 bar) the infrared spectrum observed corresponds to the expected propionylrhodium tetracarbonyl. At low partial pressure of CO (3 bar), however, the observed new spectrum was tentatively assigned to ethyl rhodium tetracarbonyl [93].

Quantum mechanical calculations at the MP4(SDQ) level were carried out to investigate the energies and reaction mechanism for the propene insertion reaction into the Rh–H bond, using the *cis*-$HRh(CO)(PPh_3)_2$ complex as a model catalytic species. The results show that the formation of the branched alkylrhodium product has an activation energy of 162 kcal mol^{-1}, and that of the straight alkylrhodium product 143 kcal mol^{-1} [94].

In situ NMR investigation of the $RhH(CO)(PPh_3)_3$-catalyzed 1-hexene hydroformylation has been made at 40 bar $CO:H_2 = 1:1$ pressure. Except for $RhH(CO)_2(PPh_3)_2$, no direct observation of labile intermediates involved in the catalytic cycle has been detected [95].

The effect of the bite angle of a series of xantphos-type ligands on the rhodium diphosphine-catalyzed 1-octene and styrene hydroformylation was investigated. Results of X-ray crystal structure and solution structure determinations of xantphos-type (diphosphine)$Rh(CO)H(PPh_3)$ complexes and of CO dissociation rates of (diphosphine)$Rh(CO)_2H$ complexes indicate that the bite angle effect on hydroformylation activity is dominated by the rates of reaction of the (diphosphine)Rh(CO)R intermediates with CO and alkene. The bite angle affects the selectivity in the steps of alkene coordination and hydride migration [96].

The ^{1}H-, ^{31}P- and ^{103}Rh-NMR spectra of a series of active hydroformylation catalysts, hydridorhodiumbis(carbonyl)diphosphine complexes have been obtained under synthesis gas pressure using a sapphire high-pressure NMR tube. The complexes exist as a mixture of equatorial–equatorial and equatorial–axial five-coordinate isomers, which are in a dynamic equilibrium. A correlation of the ^{103}Rh chemical shift with the ligand basicity was found [97].

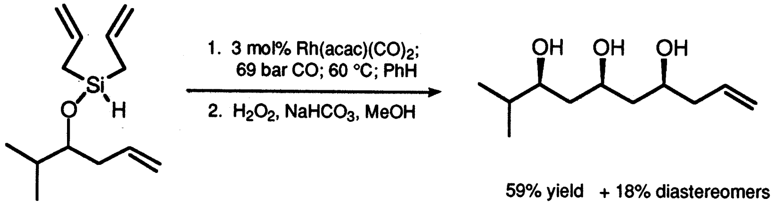
A theoretical study of the mechanism of carbonyl insertion reaction on the model system $CH_3Ni(CO)_2Cl$ reacting with a CO molecule has been made using a density function theory approach. It was found that two different pathways lead to the acyl complexes. Along one reaction channel the carbonyl insertion takes place on a five-coordinated intermediate, while the other reaction channel involves the formation of four-coordinated complexes. The two reaction pathways require the overcoming of similar energy barriers for the CO insertion process. The computational results suggests that for the real system the two reaction paths can become highly competitive and their relative importance can change depending on the experimental conditions [98].

Quantum mechanical calculations were carried out at the MP4(SDQ)//MP2 level of theory to determine the energies and reaction mechanism for the carbonyl insertion reaction using heterobimetallic $Pt(SnCl_3)(PH_3)_2(CO)CH_3$ complex as a model catalytic species. The results show that this reaction proceeds through a three-center transition state, with an activation energy of 26.4 kcal mol^{-1}, followed by an intramolecular rearrangement to the square-planar *cis*-$Pt(SnCl_3)(PH_3)_2$-(CH_3CO) metal-acyl product [99].

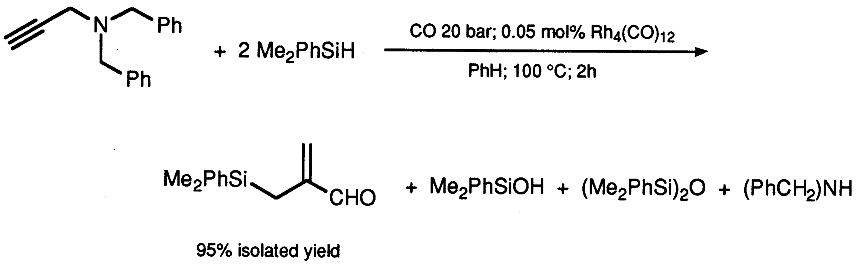
2. Hydroformylation related reactions of CO

2.1. Silylformylation

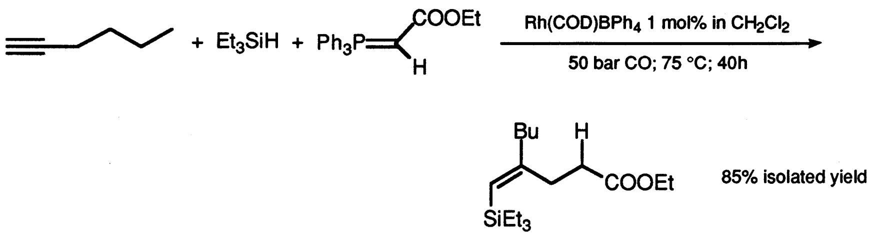
Intramolecular silylformylation of diallylsilane combined with spontaneous intramolecular aldehyde allylsilylation and subsequent oxidation led to a mixture of triols in good yields [100]. E.g.:



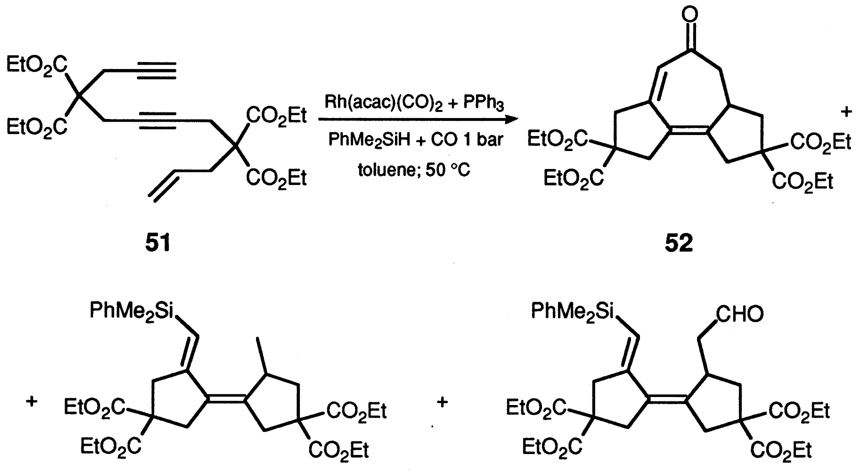
A facile route to form 2-silylmethyl-2-alkenals in a $Rh_4(CO)_{12}$-catalyzed reaction of a 2-propylamine derivative with two equivalents of trialkylsilane was reported. [101]. E.g.:



The sequential silylformylation/Wittig olefination of terminal alkynes with hydrosilanes and carbon monoxide using $Rh(COD)BPh_4$ or $Rh(CO)_2(acac)$ and $P(OPh)_3$ as the precatalyst led to substituted 2,4-dienoic esters in a one-pot procedure with high (2*E*,4*Z*) stereoselectivity [102]. E.g.:

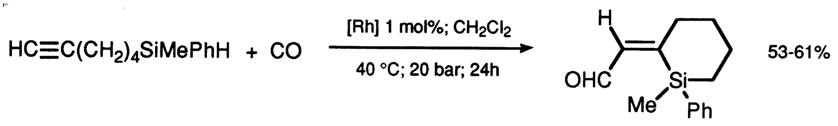


The reaction of enediyne **51** with $PhMe_2SiH$ catalyzed by $Rh(acac)(CO)_2 + PPh_3$ at 50°C under 1 bar CO gave a product in 52% yield with a product ratio of 52:53:54 = 10:32:58. The effect of the reaction condition on the product ratio with various substituted enediynes has been studied [103].



53 **54**

The rhodium-catalyzed intramolecular silylformylation of substituted ω-silylacetylenes was studied. At 40°C and 20 bar CO pressure in the presence of 1 mol% rhodium complex ($Rh^+(C_7H_8)BPh_4^-$, $Rh(CO)_2(acac)$ or $Rh_4(CO)_{12}$, 6-(methylphenylsilyl)-1-hexyne gave regioselectively **55** in 53–61% isolated yield. The presence of a C3-substituent (Me or ^{t}Bu) on the ω-silylacetylenic precursor does not affect the regioselectivity of the reaction. In the case of the bulkier substituent (^{t}Bu) the formation of only one diastereoisomer 56 was detected [104].



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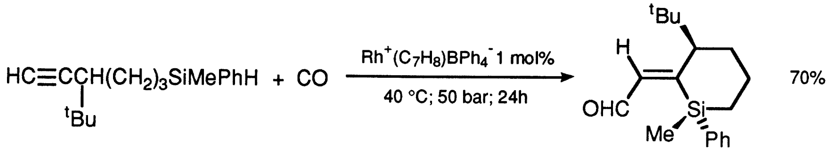


56

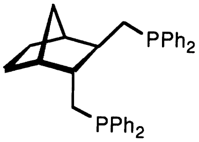
2.2. *Hydrocarboxylation, alkoxycarbonylation, thioformylation, and amidocarbonylation*

The mechanism of hydrocarboxylation of olefins using $Co_2(CO)_8$ as the catalyst precursor was discussed on the basis of published data on stoichiometric and catalytic hydrocarboxylation of a series of olefins [105].

Bimetallic rhodium carbonyl complexes with P,S-chelating, *o*-carboranylphosphinothiolato ligands were found to be more effective in catalyzing the carbonylation of methanol to acetic acid than the previously known catalyst, $[RhI_2(CO)_2]^-$. At equivalent rhodium catalyst concentrations 2.71 times higher turnover number was observed in the case with the rhodium dimer containing the bulky *o*-carborane ligand than with $[RhI_2(CO)_2]^-$ at 48 bar and 180°C [106].

The use of the ChemNet computer program, designed for mechanistic studies of organic reactions occurring in solutions of metal complexes and on the surface of heterogeneous catalysts, was illustrated by applications among others to catalyzed homogeneous hydrocarboxylation and hydroformylation of ethene [107].

Palladium catalyst systems based on *exo,endo*-2,3-bis(diphenylphosphinomethyl)-norbornane (**57**) were found to be highly active and selective for the production of methyl propanoate ($>90\%$) [108].

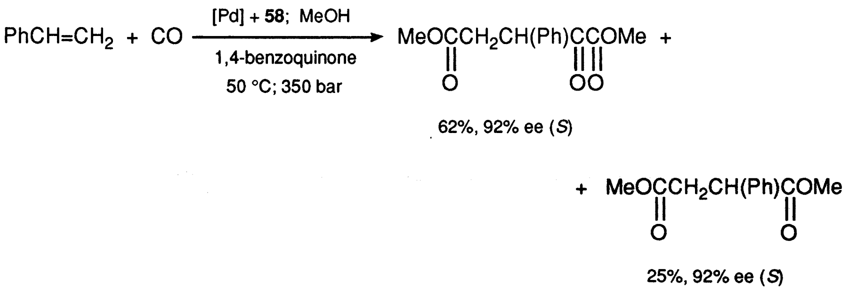


57

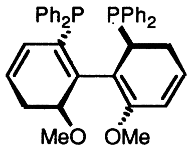
Hydrocarboxylation of styrene using various mono- and diphosphine-modified palladium catalysts was investigated. Catalysts containing monophosphines as ligands give 2-phenylpropanoic acid as the major product and the 3-phenylpropanoic acid is obtained when diphosphines are used [109].

The critical role of the counter anion in the hydroxycarbonylation of styrene for different phosphorus-modified palladium systems has been discussed [110]. The hydrocarboxylation of acenaphthylene with the $[PdCl_2(CH_3CN)_2] + 4P(C_6H_4\text{-}4\text{-}F)_3$ catalytic system was found to give acenaphthene-1-carboxylic acid in 74% yield at 80°C and 30 bar CO pressure in the presence of oxalic acid [111].

The multiple carbonylation of 1-olefins (styrene, propene, 3-phenyl-1-propene, and 4-methyl-1-pentene) to 2-oxopentanedioates and to butanedioates catalyzed by cationic palladium (II) complexes in the presence of an oxidant such as 1,4-benzoquinone has been studied. The triple carbonylation was found to be regiospecific for styrene, whereas the possible regioisomers are formed for the aliphatic olefins. Using the catalyst precursor $[\{(S)\text{-MeO–BIPHEP}\}Pd(H_2O)_2](BF_4)_2$, (S)-MeO–BIPHEP $=$ **58** in the multiple carbonylation of styrene enentioselectivities up to 93% of the products were observed [112]. E.g.:

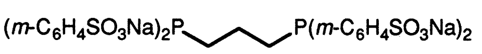


$$\mathrm{PhCH{=}CH_2 + CO \xrightarrow[\substack{1,4\text{-benzoquinone}\\ 50\ ^\circ C;\ 350\ bar}]{[Pd] + \mathbf{58};\ MeOH} MeO\underset{\underset{O}{\|}}{C}CH_2CH(Ph)\underset{\underset{O}{\|}}{C}\underset{\underset{O}{\|}}{C}OMe + MeO\underset{\underset{O}{\|}}{C}CH_2CH(Ph)\underset{\underset{O}{\|}}{C}OMe}$$



58

Water-soluble palladium complexes with sulfonated the diphosphines DPPPTS (**59**), (*S*,*S*)-BDPPTS (**60**), DPPBTS (**61**) and (*R*,*R*)-CBDTS (**62**) were found to be active in the catalytic hydrocarboxylation of neat vinyl arenes (styrene, 4-methoxystyrene, 4-fluorostyrene) under biphasic conditions without addition of an acid and an organic solvent. However, the stability of the catalyst systems increases when the reaction is performed in an acidic medium (pH ~ 3.5 with H_2SO_4). The catalysts could be recycled twice with no loss in activity. In the case of the $[Pd(OAc)_2]/60$ system at 100°C and 20 bar CO pressure at complete conversion of 4-methoxy-styrene, 45% of branched product and enantioselectivities up to 43% are obtained [113].



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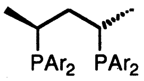

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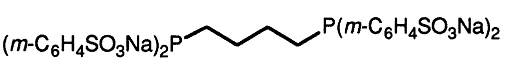

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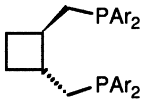
Ar = *m*-$NaO_3SC_6H_4$



62

A novel water-soluble palladium complex containing pyridine carboxylate and TPPTS as ligand was found to be a highly active catalyst at 115°C and 54 bar CO pressure for the carbonylation of vinyl aromatics (styrene, 4-isobutylstyrene, 4-*tert*-butylstyrene, 6-methoxy-2-vinylnaphthalene) under biphasic conditions and provides high regioselectivity (up to 98%) to 2-arylpropionic acids [114].

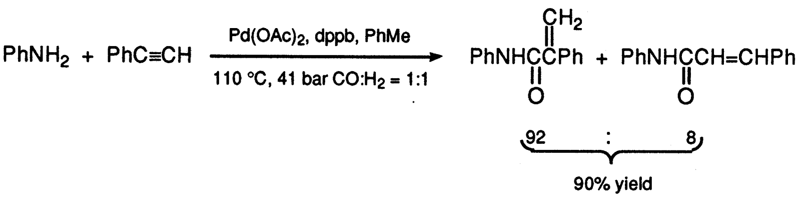
The kinetics and mechanism of styrene hydroalkoxycarbonylation catalyzed by the complex $PdCl_2(Ph_3P)_2$ in the presence of butanol were studied in dioxane at 110°C. Based on the isolation of the acyl complex $PhC_2H_4C(O)PdCl(Ph_3P)_2$ from the reaction mixture the hydride mechanism of styrene hydrocarboxylation has been assumed [115].

Alkoxycarbonylation of styrene using an in situ-formed palladium complex catalyst, $Pd(OTs)_2(PPh_3)_2$, was investigated. The effect of various ligands, promoters, solvents and alcohols on the catalytic activity as well as the selectivity pattern was studied. It was found that the regioselectivity to the branched product, 2-phenyl propionate, increases with decrease in basicity of the phosphorus ligands as well as steric bulk around the palladium center and polarity of the medium [116].

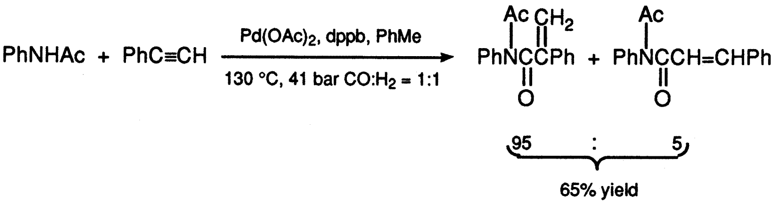
The mechanism of styrene hydroesterification using in situ-formed $Pd(OTs)_2(PPh_3)_2$, from $Pd(OAc)_2$, PPh_3 and TsOH in methanol was investigated by isolation and spectroscopic characterization of catalytically active hydrido- and acyl-palladium intermediates [117].

The dinuclear palladium complex, *cis*-[chlorotriphenylarsino-palladium(I)-(μ-carbonyl)chlorotriphenylarsinopalladium(I), was found to exhibit catalytic activity in acetylene alkoxycarbonylation [118].

The carbonylative coupling of aniline derivatives with terminal aryl acetylenes catalyzed by $Pd(OAc)_2$ and 1,4-bis(diphenylphosphino)butane under 41 bar syngas pressure affords acrylamide derivatives in excellent yields and selectivities [119]. E.g.:



$$\mathrm{PhNH_2 + PhC{\equiv}CH \xrightarrow[110\ ^{\circ}C,\ 41\ bar\ CO:H_2\ =\ 1:1]{Pd(OAc)_2,\ dppb,\ PhMe} \underbrace{PhNH\underset{\underset{O}{\|}}{C}\overset{\overset{CH_2}{\|}}{C}Ph + PhNH\underset{\underset{O}{\|}}{C}CH{=}CHPh}_{\substack{92\ :\ 8\\ 90\%\ yield}}}$$

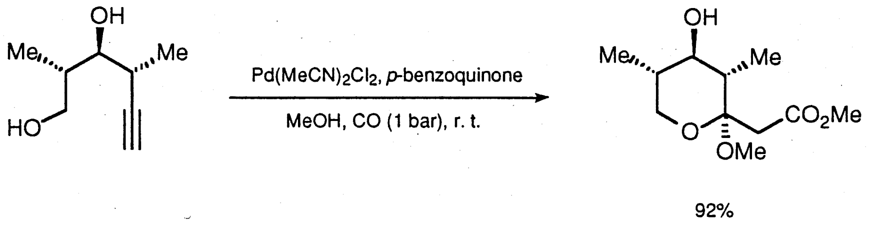


$$\mathrm{PhNHAc + PhC{\equiv}CH \xrightarrow[130\ ^{\circ}C,\ 41\ bar\ CO:H_2\ =\ 1:1]{Pd(OAc)_2,\ dppb,\ PhMe} \underbrace{Ph\overset{\overset{Ac}{|}}{N}\underset{\underset{O}{\|}}{C}\overset{\overset{CH_2}{\|}}{C}Ph + Ph\overset{\overset{Ac}{|}}{N}\underset{\underset{O}{\|}}{C}CH{=}CHPh}_{\substack{95\ :\ 5\\ 65\%\ yield}}}$$

Palladium(II) acetate in combination with tri(2-furyl)phosphine and methanesulfonic acid was found to be an efficient catalyst for the alkoxycarbonylation of phenylacetylene at 50–80°C and 20 bar CO pressure leading with high regioselectivity (95%) to the formation of 2-phenyl acrylic ester [120].

Palladium(II) and rhodium ions, or palladium complexes with bidentate *N*-donor ligands such as 2,2′-bipyridyl and 1,10-phenanthroline, intercalated in the layers of zirconium hydrogen phosphate were found to catalyze both single and double methoxo carbonylation of phenylacetylene [121].

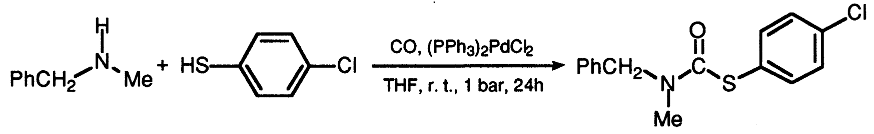
Treatment of δ-hydroxy alkynes with 5 mol% $Pd(MeCN)_2Cl_2$ in methanol containing 1.1–1.5 equivalents of *p*-benzoquinone under 1 bar of CO was found to afford methyl ketopyranosides with excellent stereoselectivity. The reaction proceeds by sequential intramolecular alkoxypalladation of the alkyne followed by CO insertion and methanolysis and an ensuing Pd^{2+}-catalyzed 1,4-addition of methanol to the intermediate conjugated ester [122]. E.g.:



The catalytic carbonylation of benzyl bromide to phenylacetic acid and its esters in the presence of water soluble palladium complexes was studied. The catalytic system consisting of $PdCl_2(COD)$ and a water-soluble phosphine, $Ph_2PCH_2CH_2C(O)NHC(CH_3)_2CH_2SO_3Li$, in water/toluene solution was found to be active for the carbonylation of benzyl bromide at 130°C and 10 bar CO pressure [123].

The carbonylation of aryl halides catalyzed by CO_2-soluble palladium complexes with trialkyl or aryl phosphite ligands was found to proceed rapidly in supercritical carbon dioxide. The rate of the reaction is higher than those obtained in solution phase reactions [124].

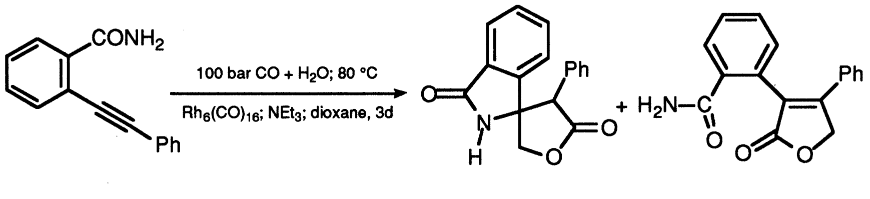
The thiocarbamate **63** has been obtained selectively in 47% isolated yield by the palladium-catalyzed carbonylation of *N*-benzylmethylamine in the presence of 4-chlorobenzenethiol at ambient temperature and pressure [125].



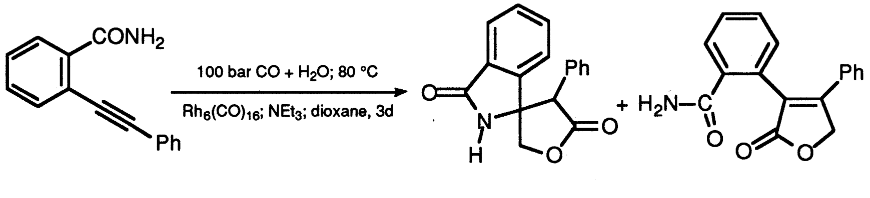
63

An examination of the palladium-catalyzed alkoxycarbonylation of 4-bromoacetophenone led under optimized conditions to catalyst productivities of up to 7000 mol product (4-*n*-butoxycarbonylacetophenone)/mol palladium. Using the system 4-bromoacetophenone/*n*-butanol/Et_3N/0.01 mol% palladium/0.8 mol% PPh_3/5 bar CO at 100–130°C enables the best catalyst performance [126].

The rhodium-catalyzed carbonylation of 2-phenylethynylbenzamide derivatives under water–gas shift reaction conditions in the presence of $Rh_6(CO)_{16}$ as the catalyst precursor gave spiro compound and 2-(5*H*)-furanone such as **64** and **65** in 34 and 45% isolated yield, respectively [127].



61 **62**



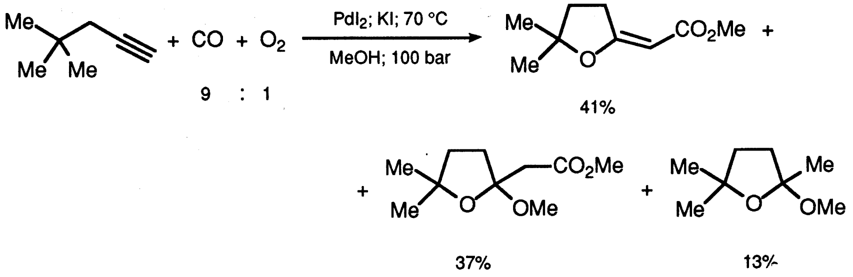
64 **65**

Synthesis and spectroscopic characterization of all the intermediates in the palladium-catalyzed methoxycarbonylation of ethene to methyl propanoate has been achieved. Based on unambiguously identified intermediates by multinuclear NMR spectroscopy and ^{13}C-labeling, the formation of methyl propanoate was shown to occur via a hydride rather than a methoxycarbonyl cycle [128].

The palladium complex $Pd(Ph_2Ppy)_2(PhC{=}CH_2)(CF_3CO_2)$ was found to be active for the catalytic methoxycarbonylation of phenylacetylene to 2-phenylpropenoate at ambient temperature under 2 bar CO pressure [129].

The preparation of pyridinecarboxylates and pyridinedicarboxylates by alkoxycarbonylation of chloropyridines with carbon monoxide in the presence of palladium acetate and 1,1′-bis(diphenylphosphino)ferrocene was investigated [130].

A direct synthesis of 2-[(methoxycarbonyl)methylene]tetrahydrofurans by palladium-catalyzed oxidative cyclization–methoxycarbonylation of readily available 4-yn-1-ols has been described [131].

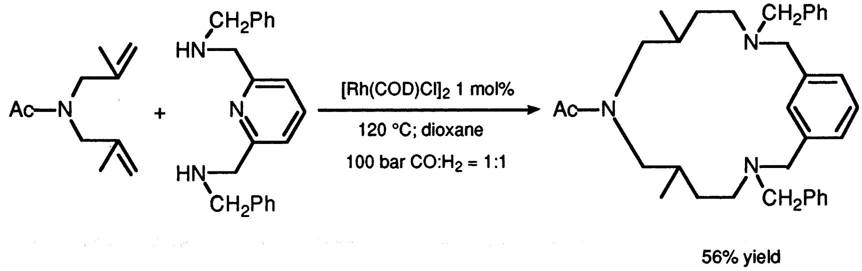


The effect of the composition of the catalytic system $Pd(dba)_2/HX/RPPh_2$ on the yield and regioselectivity of the reaction of phenylacetylene with carbon monoxide and *n*-butanol in toluene was studied. The highest yield of butyl 2-phenylpropenoate and butyl 3-phenylpropenoate was obtained at $X = CF_3COO$, and the activity of the catalyst decreases with X in the order $CF_3COO > p\text{-}TsO > BF_4 \geq ClO_4 > CF_3SO_3 > ClCH_2COO > AcO \approx Cl$ and with R in the order $Ph > 2\text{-}py > Ph_2PC_2H_4 > Ph_2P(O)C_2H_4 > Et$ [32].

See also Refs. [25,56,98].

2.3. Hydroaminomethylation

A new and versatile access to polyazomacrocycles and cryptands through ring-closing bis(hydroaminomethylation) has been disclosed. Starting from (hetero)diallylic systems, the rhodium(I)-catalyzed hydroformylation in the presence of primary amines or secondary α,ω-diamines lead to 12- to 36-membered polyheterocycles in up to 56% yield [133]. E. g.:



The rhodium-catalyzed hydroaminomethylation of unsaturated fatty acid derivatives, oleic acid ethyl ester and oleyl alcohol with primary and secondary amines has been studied [134].

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

The H_2 generated in situ from H_2O via the water gas shift reaction in the presence of phosphomolybdic acid has been applied for the catalytic desulphurization of benzothiophene in a water/toluene emulsion [135].

The kinetics of the catalytic reduction of nitrobenzene to aniline in aqueous 2-picoline under water gas shift reaction conditions in the presence of *cis*-$[Rh(CO)_2(2\text{-picoline})_2]PF_6$ were studied. The rate of nitrobenzene reduction shows a first-order dependence on carbon monoxide pressure over the range of 0–1.9 bar at 80, 100 and 120°C. The catalytic activity was found to be non-linear in total rhodium concentration over the range of 5–60 mM [136]. The effect of temperature on the water–gas shift reaction catalyzed by poly(4-vinylpyridine) immobilized $[Rh(COD)(4\text{-picoline})_2]PF_6$ was studied under continuous-flow conditions at 100–180°C. The temperature dependence was found to follow a segmented Arrhenius behavior. The immobilized catalyst was also characterized by DTA-TGA analysis, FT-IR, UV–vis reflectance, electron paramagnetic spectroscopy and X-ray photoelectron spectroscopy [137]. Kinetics of the water gas shift reaction catalyzed by $[Rh(COD)(4\text{-picoline})_2]PF_6$ immobilized on poly(4-vinylpyridine) 2% cross linked with divinylbenzene in contact with a mixture of 80% aqueous 2-ethoxyethanol were studied. The results show a first order dependence on carbon monoxide pressure and a nonlinear dependence on the total rhodium concentration [138].

Rhodium(I) amino complexes immobilized on poly(4-vinylpyridine) were used as catalysts in the reduction of nitrobenzene to aniline in contact with 80% aqueous 2-ethoxyethanol under water gas shift conditions (0.9 bar of CO pressure at 100°C, nitrobenzene/Rh = 25). Aniline is observed with a 99% selectivity. Among the catalysts studied $[Rh(COD)(2\text{-picoline})_2][PF_6]$/poly(4-vinylpyridine) system appears to be the most active (53 mol aniline/mol Rh/day) [139].

Homogeneous catalysts for the water–gas shift reaction prepared from $Rh_2(\mu\text{-}Pz)_2(COD)_2$ (Pz = pyrazolate ion, COD = 1,5-cyclooctadiene) in aqueous pyridine, 4-picoline or 2-ethoxyethanol and $Rh_2(\mu\text{-}Pz)_2(CO)_2(TPPMS)_2$ (TPPMS = *meta*-sulfonatophenyl–diphenylphosphine) in acidic aqueous media under mild conditions were described. These complexes also catalyze the reduction of nitrobenzene to aniline [140].

The catalytic system $PdCl_2/Fe/I_2$/pyridine/ethanol for nitrobenzene reductive carbonylation to ethyl phenylcarbamate was investigated. At. 180°C under 40 bar CO pressure 83.4% ethyl phenylcarbamate and 14% aniline was obtained at 99.6% nitrobenzene conversion [141].

The effect of the tetraethylammonium chloride on the mechanism of the $Ru_3(CO)_{12}$-catalyzed carbonylation of nitroarenes to carbamates has been investigated [142].

2-Hydroxypyridine and related molecules were found to have a large activating effect on the [PPN][$Rh(CO)_4$]-catalyzed carbonylation of nitrobenzene to methyl phenylcarbamate without any loss in selectivity [143].

Identification of reaction intermediates in the water–gas shift reaction on zeolite-encapsulated gold catalysts have been studied by means of in situ FT-IR spectroscopy. Exposure of Au^{n+}/zeolites to a gas mixture of $CO + H_2O$ at 323 K produced IR carbonyl spectra of Au–CO species and a unidentate formate species [144].

See also Refs. [4,127].

2.5. Reduction of CO and CO_2

Hydrogenation of carbon dioxide by the complex $(CpTi)_2(\mu\text{-}H)_2(\mu\text{-}C_{10}H_8)$ affords methanol after protonation with HCl [145].

Ruthenium-catalyzed hydrogenation of carbon dioxide into formic acid was theoretically investigated with the DFT (B3LYP) method using *cis*-$RuH_2(PH_3)_4$ as a catalyst model. The calculations have shown that CO_2 insertion into the Ru–H bond occurs with an activation energy of 29.3 kcal mol^{-1} in *cis*-$RuH_2(PH_3)_4$ and with 10.3 kcal mol^{-1} in *cis*-$RuH_2(PH_3)_3$. A six-membered sigma-bond metathesis of $RuH(\eta^1\text{-}OCOH)(PH_3)_3H_2$ was found to be very favorable with an E_a value of 8.2 kcal mol^{-1}. Therefore, if PH_3 dissociates from *cis*-$RuH_2(PH_3)_4$, the CO_2 hydrogenation takes place through the CO_2 insertion into the Ru–H bond of $RuH_2(PH_3)_3$ followed by the six-membered sigma-bond metathesis, where the rate-determining step is the CO_2 insertion. If PH_3 does dissociate from *cis*-$RuH_2(PH_3)_4$ and *cis*-$RuH(\eta^1\text{-}OCOH)(PH_3)_4$, the CO_2 hydrogenation proceeds through the CO_2 insertion into the Ru–H bond of *cis*-$RuH_2(PH_3)_4$ followed by the H–OCOH reductive elimination, where the rate-determining step is the CO_2 insertion [146].

Reduction of CO_2 in γ-ray irradiated CO_2-water systems were investigated in the presence of various metal powders, metal oxides, metal ions, and inorganic anions. It was found that Cu^{2+} and SO_3^{2-} have a 100-fold enhancing effect in CO production. The CO production is 2–14 times higher in the presence of the additives such as $NiSO_4$, $ZnSO_4$, Ag_2SO_4, $MnCl_2$, $CoCl_2$, $FeSO_4$ and $CuSO_4$. The largest concentration of CO was detected when Cu^{2+} and SO_3^{2-} were present together in the irradiated reaction mixture. The enhancing factor was found to be about 100-fold comparing to the system without them [147].

A stable catalytic system was obtained by immobilizing nickel(II) and (2,2′-bypyridine)ruthenium(II) complexes into a Nafion membrane for the photocatalytic reduction of carbon dioxide to formic acid [148].

Cyclic voltametry and controlled potential electrolysis techniques were employed to investigate the electrochemical reduction of carbon dioxide to carbon monoxide and trace amounts of formic acid using nickel(II) macrocyclic complex of 1,8-diethyl-1,3,6,8,10,13-hexaazacyclotetradecane. The product selectivity was found to be influenced by the pH [149].

Macrocyclic nickel(II) complexes were found to be active and persistent redox catalysts for the electrochemical reduction of CO_2 to oxalate [150].

The role of C–H bond formation in the reduction of carbon dioxide mediated by palladium phosphine catalysts has been studied [151].

3. Reviews

1. Ligand bite angle effects in metal-catalyzed C–C bond formation. A review with 285 references [152].

2. Silicometallics and catalysis. A brief review among others about silylformylation of acetylene by transition metal complexes with 97 references [153].

3. Controlling stereoselectivity with the aid of a reagent-directing group: hydroformylation, cuprate addition, and domino reaction sequences. Based on several examples the concept of controlling stereoselectivity with the aid of a reagent directing group such as the *ortho*-diphenylphosphanylbenzoate in substrate-directed stereoselective hydroformylation of methallylic and homomethallylic alcohol derivatives has been elucidated with 61 references [154].

4. Carbon dioxide as an environmentally benign reaction medium for chemical synthesis. A review with 38 references of the research efforts of the Max-Planck-Institute for Coal Research concerning the use of compressed (liquid or supercritical) carbon dioxide as a solvent for environmentally friendly synthesis of fine chemicals among others in transition metal-catalyzed asymmetric C–C bond forming reactions [155].

5. Homogeneous catalysts for application in supercritical carbon dioxide as a ‘green’ solvent. A review with 45 references about various approaches by which homogeneous catalytic systems were successfully adjusted to the special solvent properties of compressed carbon dioxide [156].

6. Room temperature molten salts: neoteric ‘green’ solvents for chemical reactions and processes. A review on the use of ionic liquids in the last two years in green technologies. More than 55 references [157].

7. The bite angle makes the catalyst. A review with 38 references on the application of bidentate phosphine ligands with wide bite angles in rhodium-catalyzed hydroformylation among others to obtain highly linear products [158].

8. Hidden catalysts unveiled. A review with 13 references about the activities of the catalyst evaluation and optimization service at the University of St. Andrews, giving examples in rhodium-catalyzed hydroformylation [159].

9. Pentacarbonylhydridochromates $M^+[HCr(CO)_5]^-$; Reactivity in organic synthesis and homogeneous catalysis. A review with 83 references among other about the role of $[HCr(CO)_5]^-$ in water–gas-shift reaction, synthesis of methyl formate and synthesis of alkyl formates [160].

10. Thermoregulated phase-transfer catalysis — recent advances in water/organic biphasic hydroformylation. A review with 36 references [161].

11. Amidocarbonylation — an efficient route to amino acid derivatives. A review of transition metal-catalyzed amidocarbonylation with 184 references [162].

12. Homogeneous catalysis with transition metal complexes. A review with 114 references [163].

13. Metal catalysis in water. A review with 132 references [164].

14. Reactions in supercritical carbon dioxide. A review with 100 references [165].

15. Modern solvent systems in industrial homogeneous catalysis. A review with 136 references [166].

16. Perspectives of rhodium organometallic catalysis. Fundamental and applied aspects of hydroformylation. A review with 78 references [167].

Acknowledgements

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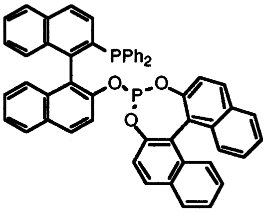
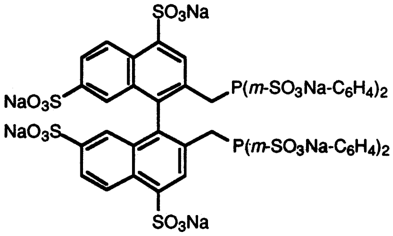
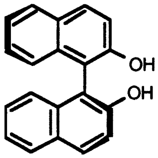
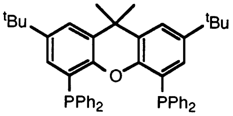
Appendix A. List of Abbreviations

Ac	acetyl
Ar	aryl
acac	acetylacetonate
BDPP	2,4-bis(diphenylphosphino0pentane
BINAP	2,2’-bis(diphenylphosphino)-1,1’-binaphthyl
BINAPHOS	
BINAS	
BINOL	

BIPHEPHOS	see **25**
Bn	benzyl
bpy	2,2′-bipyridine
Bu	butyl
Bz	benzoyl
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
cyclam	1,4,8,11-tetraazacyclotetradecane
dba	dibenzylideneacetone
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DMA	*N*,*N*-dimethylacetamide
DMF	*N*,*N*-dimethylformamide
DMSO	dimethylsulfoxide
DPPB	$Ph_2PCH_2CH_2CH_2CH_2PPh_2$
DPPE	$Ph_2PCH_2CH_2PPh_2$
DPPP	$Ph_2PCH_2CH_2CH_2PPh_2$
ee	enantiomeric excess
Et	ethyl
^{c}Hx	cyclohexyl
IR	infrared
Me	methyl
NBD	norbornadiene
Ph	phenyl
Phen	1,10-phenanthroline
py	pyridine
sc	supercritical
THF	tetrahydrofuran
TN	turnover number (mol product/mol cat)
TOF	turnover frequency (mol product/mol cat/time)
TPPMS	sodium-*m*-(diphenylphosphino)benzene sulfonate
TPPTS	trisodium salt of the trisulfonated triphenylphosphine
Ts	*p*-toluenesulfonyl (tosyl)
Xantphos	

Appendix B. The metals and their associated references

Metal	Refs.
Ti	[8,145]
Zr	[53,121]
Cr	[160]
Mo	[135]

Mn	[147]
Fe	[23,24,52,54,56,141,147]
Ru	[142,146,148]
Co	[1,2,62,88–91,105,147,162]
Rh	[3–51,53,54,58,62–88,92–97,100–104,106,121,127,133,134,136–140,143,152,155,158,159,161,167]
Ir	[106]
Ni	[98,147–150]
Pd	[25,55,56,107–126,128–132,141,151,152,162]
Pt	[56–61,99]
Cu	[147]
Ag	[147]
Au	[144]
Zn	[147]
Sn	[57–60,99]

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