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Review

# Application of transition metals in hydroformylation Annual survey covering the year 2006

Ferenc Ungváry [*]

*Department of Organic Chemistry, University of Veszprém, Egyetem u. 10, H-8200 Veszprém, Hungary*

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## Contents

## Abstract

Hydroformylation in homogeneous and heterogeneous systems, and hydroformylation related reactions of carbon monoxide reported in 2006 are reviewed.

*Keywords:* Hydroformylation; Silylformylation; Hydroxycarbonylation; Alkoxycarbonylation; Hydroaminomethylation; Transition metals

## 1. Hydroformylation

### 1.1. Homogeneous systems

### 1.1.1. Cobalt catalysts

Thermodynamic parameters relevant to the phosphine-modified cobalt-catalyzed hydroformylation reaction were reported. Thus, equilibrium constants for the hydrogenation of

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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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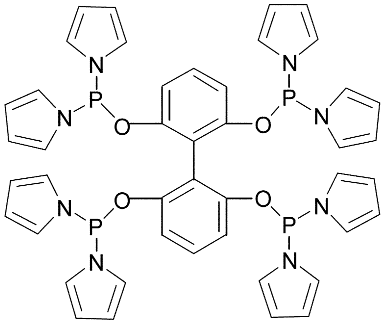
$Co_2(CO)_6L_2$ to yield $HCo(CO)_3L$ (L = *tert*-phosphines) were determined using in situ $^1H$ and $^{31}P$ NMR spectroscopy between 75 and 175 °C for various solvents and phosphine ligands. Based on analysis of the $^{31}P$ NMR line width lower limits were established for the catalytically relevant Co–Co and Co–H bond energies in the case of $L = {}^nBu_3P$ (Co–Co $\geq$ 23 kcal/mol and Co–H $\geq$ 60 kcal/mol) relative to the previously reported values for the case of L = CO (Co–Co = 19 ± 2 kcal/mol and Co–H = 59 ± 1 kcal/mol) [1] (see also Ref. [130]).

### *1.1.2. Rhodium catalysts*

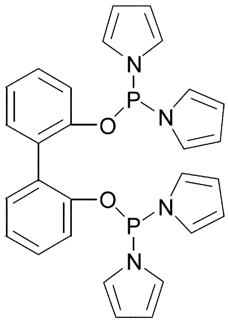
The unmodified rhodium-catalyzed hydroformylation of 2-phenylsulfonylbicyclo[2.2.1] alkenes was investigated. It was found that the steric properties of the sulfonyl substituent, more than the electronic ones, influence the regioselectivity of the process [2].

The synthesis and the catalytic activity in the rhodium-catalyzed hydroformylation of styrene as well as quantum-chemical estimation of structure–activity relationship of novel cyclic amidophosphonite ligands bearing polyfluorinated tails were reported [3]. The origin of stereo induction by chiral aminophosphane phosphinite ligands in asymmetric hydroformylation was investigated with a theoretical approach using density functional calculations and hybrid QM/MM calculations. Results indicate that alkene insertion into the rhodium–hydride bond is the selectivity-determining step, and not alkene coordination [4].

The catalytic properties of rhodium complexes containing alpha-, beta-, or gamma-aminophosphine ligands in styrene hydroformylation were examined. The results show that the activity increases when the number of backbone carbon atoms linking P and N decreases from 3 to 1 [5]. Higher regioselectivity was achieved in the rhodium-catalyzed isomerization–hydroformylations of internal olefins using a new pyrrol-based tetraphosphorus ligand **1** compared with its biphosphorus analogue **2**. Normal:iso values up to 80.6 from 2-hexene and up to 51.7 from 2-octene were achieved with this catalytic system using a ligand/rhodium ratio of 3, a substrate/catalyst ratio of 10,000, at 100 °C and 10 bar $CO:H_2 = 1:1$ [6].

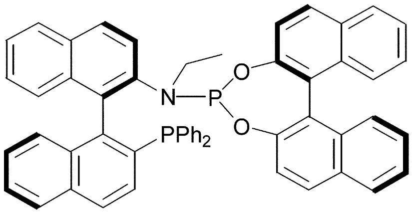


**1**



**2**

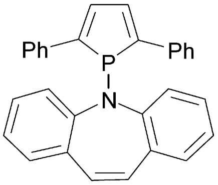
Excellent enantioselectivities (up to 99% ee) were achieved in the rhodium-catalyzed asymmetric hydroformylation of styrene derivatives and vinyl acetate at 40 °C and 20 bar $CO:H_2 = 1:1$ using a new hybrid phosphorus ligand **3** [7].



**3**

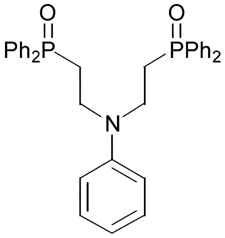
Chiral spiro phosphoramidite ligands were found to be efficient in rhodium-catalyzed asymmetric hydroformylation of styrene to give excellent yields and regioselectivities but only modest level of enantioselectivities [8].

The activity of rhodium complexes as catalysts with a new aminophosphole ligand (**4**) was tested for hydroformylation of mono- and disubstituted olefins [9].



**4**

A new rhodium complex with a nitrogen-containing bis(phosphine oxide) ligand (**5**) was applied to hydroformylation of styrene. High activity (TON up to 1443 mol aldehyde/mol catalyst) and regioselectivity towards the branched aldehyde (96.9%) was found at 30–40 °C and 20–100 bar $CO:H_2 = 1:1$ [10].

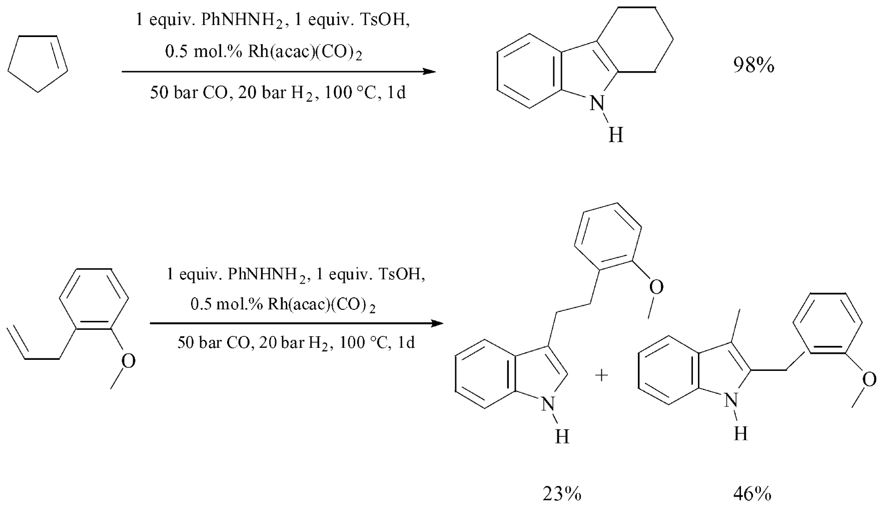


**5**

Highly regioselective hydroformylation of unsaturated esters was achieved when a reactive, ligand-modified rhodium catalyst was employed near ambient temperatures (15–50 °C) and pressures over 30 bar. The use of 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantane was found to show distinct advantages over other commonly applied phosphines in terms of reaction rate, and regio- and chemoselectivity. Hydroformylation of 1,1-di- and 1,1,2-trisubstituted unsaturated esters using this catalytic system yields quaternary aldehydes [11].

3-Hydroxy-2-methylpropionamide was obtained with up to 100% conversion and up to 97% selectivity from acrylamide by a tandem hydroformylation–hydrogenation sequence at 60 °C and 95 bar $CO:H_2 = 1:1$ and 70 °C, 95 bar $H_2$ catalyzed by $Rh(acac)(CO)_2/PPh_3 = 1:7$ and Raney Ni, respectively [12].

The tandem hydroformylation-Fischer indolisation protocol has been used in the synthesis of 2,3-disubstituted indoles. Several olefins, bearing substituents with various functional groups, as well as cyclic olefinic systems were investigated [13]. For example:



Rhodium-based catalysts have been prepared through the solid-phase reaction of catalyst precursors in supercritical carbon dioxide and evaluated for the hydroformylation of styrene to produce 2-phenylpropionaldehyde. Triphenylphosphine and (*R*)-BINAP were tested as ligands, and their effects on the reaction were examined [14].

A simple and novel method for the synthesis of a variety of 3-substituted furans by the hydroformylation of substituted propargylic alcohols was described using rhodium acetate and triphenylphosphine in dichloromethane [15].

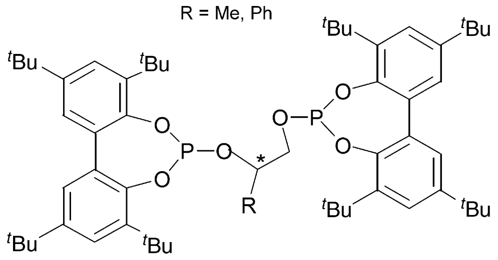
1-Octene, 1-decene and styrene were hydroformylated in supercritical carbon dioxide using a $CO_2$-philic fluorous ligand associated with a rhodium catalyst. The effect of P/Rh molar ratio, partial pressure of $CO/H_2$ and the total pressure of carbon dioxide were studied [16]. The rhodium-catalyzed hydroformylation of 1-octene with the new P-donor ligands $PPh_{3-n}(OC_9H_{19})_n$ ($n = 3, 2, 1$) containing branched alkyl chains was investigated in supercritical carbon dioxide and toluene as solvents. The selectivities for aldehydes were found to be higher in the supercritical medium than in toluene [17].

The rhodium-catalyzed hydroformylation of *m*-diisopropenylbenzene and 1-isopropyl-3-isopropenylbenzene was investigated using homogeneous and biphasic reaction conditions or silica immobilized rhodium complexes as the catalyst [18]. The rhodium-catalyzed hydroformylation of higher olefins ($>C_6$) was investigated in a $HRh(CO)(PPh_3)/P(OPh)_3$/propylene carbonate/*n*-heptane catalytic system. Normal/iso ratios >8, and efficient recycling of the catalyst was demonstrated [19].

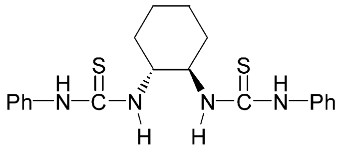
A rhodium–calix[6]arene diphosphite complex was used as a catalyst in the hydroformylation of linear alkenes, and styrenes. The influence of P/Rh and substrate/catalyst ratios, as well as temperature and pressure, on the aldehyde yield and the regioselectivity of the process was studied [20].

The rhodium precursor $[Rh(COD)Cl]_2$ complexed on phosphonated dendronized magnetic nanoparticles was found to be highly branched-selective hydroformylation catalyst for various vinyl arenes. At 50 °C and 69 bar $CO:H_2 = 1:1$ up to 100:1 = branched:linear ratios were achieved [21].

New non-C-2-symmetric chiral diphosphites (**6**) were synthesized and used as ligands in the rhodium-catalyzed enantioselective and regioselective hydroformylation of styrene. A synergistic effect improving both activity and enantioselectivity was observed when a chiral dithiourea such as **7** was introduced as co-ligand in the rhodium–diphosphite catalytic system [22].



**6**

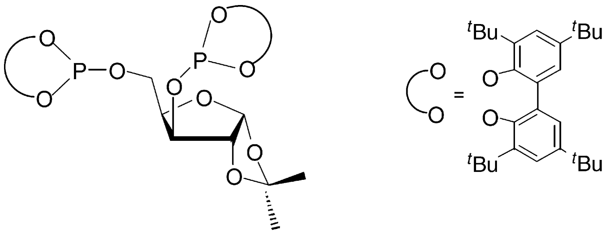


**7**

Chiral phospholane based rhodium catalysts were found to be effective in hydroformylation applications such as the formation of chiral cyclic amino acids from dieneamide esters, and the formation of chiral oxo-aldehydes from [2.2.1]-bicyclic alkenes [23].

A comprehensive theoretical investigation on the mechanism of hydroformylation and hydrogenation of propyne catalyzed by the modified catalyst $HRh(CO)_2(PH_3)$ was carried out employing a nonlocal density functional method (B3LYP). It was found that the propyne insertion into the Rh–H bond step is irreversible and that the energy barrier for hydroformylation of propyne is lower than that of hydrogenation [24].

The asymmetric hydroformylation reaction of allylbenzenes and propenylbenzenes were studied using rhodium–chiral diphosphite catalytic systems with ligands such as **8**. The diphosphine ligand **8** was found to give high regioselectivities in *trans*-anethole hydroformylation, but only low enantioselectivities [25].



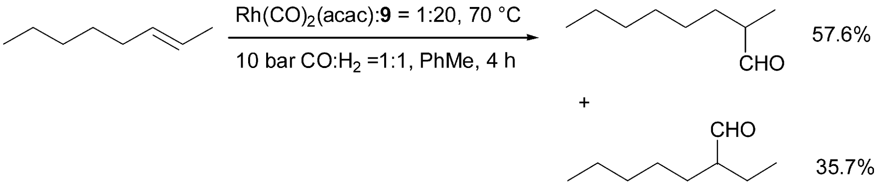
**8**

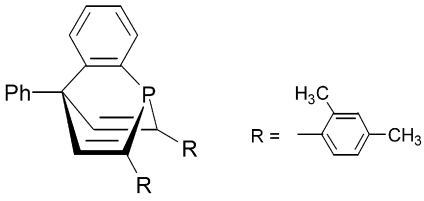
Carbon dioxide-expanded liquids were demonstrated to be effective reaction media for rhodium-catalyzed hydroformylation of 1-octene. The performance of several rhodium catalysts, Rh(acac)(CO)$_2$, Rh(acac)[P(OPh)$_3$]$_2$, Rh(acac)(CO)[P(OAr)$_3$], and two phosphorous ligands, PPh$_3$ and BIPHEPHOS, was compared in neat organic solvents and in carbon dioxide-expanded liquids wherein more than 50% of the solvent volume is replaced with dense CO$_2$ at relatively mild temperatures (30–90 °C) and pressures (<120 bar). For all catalysts, enhanced turnover frequencies were observed in carbon dioxide-expanded liquids. For the most active catalyst, Rh(acac)(CO)$_2$ modified by BIPHEPHOS ligand, the selectivity to aldehyde products was improved from approximately 70% in neat solvent to nearly 95% in carbon dioxide-expanded media [26]. Hydroformylation of propene was carried out in supercritical carbon dioxide + water and in supercritical propene + water mixtures using Rh(acac)(CO)$_2$ and P($m$-C$_6$H$_4$SO$_3$Na)$_3$ as catalyst [27].

The hydroformylation of linaool using [Rh(COD)(OAc)$_2$] as a catalyst precursor in the presence of triphenylphosphine or various diphosphines was studied. In comparison with unmodified catalyst systems the addition of (di)phosphine was found to exert a great accelerating effect so that under optimized conditions at 40–50 °C and 20 bar CO:H$_2$ = 1:1 a virtually complete conversion of linaool is achieved in 4–6 h [28]. Hydroformylation of alkenes in the presence of RhCl(PPh$_3$)$_3$ and XANTPHOS at 2.9 bar CO:H$_2$ = 1:1 was found to be complete after 4 min of microwave irradiation with high conversion into the corresponding aldehyde without formation of isomerized alkene [29].

Two different in situ prepared catalysts generated from Rh(CO)$_2$(acac) and trifluoromethyl-substituted triphenylphosphine ligands were evaluated for their activity and selectivity in the hydroformylation of 1-octene. The highest value for the turnover frequency, 9820 mol (1-octene)/mol (Rh) h, was obtained in supercritical carbon dioxide using P[C$_6$H$_3$-3,5-(CF$_3$)$_2$]$_3$ as the ligand [30].

Pocket-shaped, calixarene-based diphosphites were tested in the rhodium-catalyzed hydroformylation of 1-octene, *trans*-2-octene, and styrene at 80 °C in toluene solution [31]. A new class of phosphabarrelene/rhodium catalysts was found to display very high activity towards hydroformylation of internal alkenes with unusually low tendency towards alkene isomerization [32]. For example:

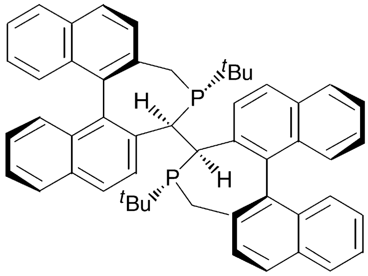




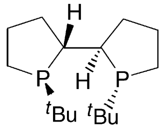
**9**

The asymmetric hydroformylation of 2- and 3-vinylfurans was investigated by using BINAPHOS-modified rhodium complexes as catalysts. Isoaldehydes were obtained in high regio- and enantioselectivities [33]. The substrate-directed asymmetric induction in the rhodium-catalyzed hydroformylation of C-allyl sugars was investigated to understand correlations between different structural features of the sugar moiety and the regio- and diastereoselectivity of the hydroformylation reaction [34].

The ligands, ($S$)-Binapine (**10**) and ($S$,$S$,$R$,$R$)-TangPhos (**11**), were found to give outstanding enantioselectivities in rhodium-catalyzed asymmetric hydroformylation of styrene (94 and 90% ee), allyl cyanide (94 and 93% ee), and vinyl acetate (87 and 83% ee) [35].



**10**



**11**

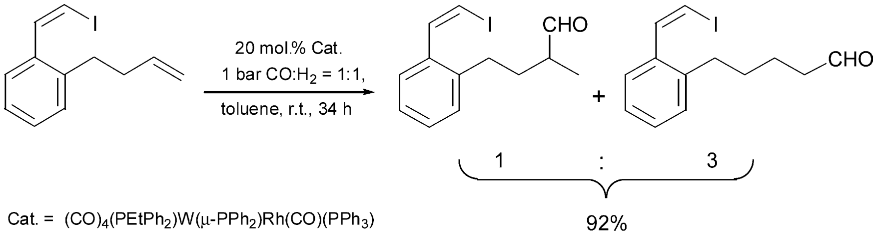
The application of chiral spiro phosphoramidite ligands in rhodium-catalyzed asymmetric hydroformylation of styrene was investigated. The alkyl groups on the amino moiety of the ligands were found to play a critical role in the control of regioselectivity and enantioselectivity of the reaction [36] (see also Refs. [47,68,74,75,130]).

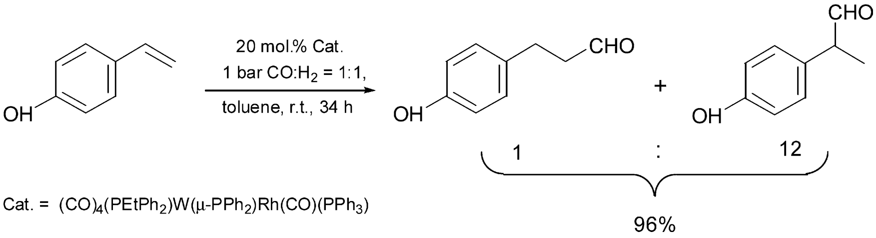
### 1.1.3. Other metals as catalysts and bimetallic catalysts

Highly selective halide anion-promoted palladium-catalyzed hydroformylation of internal alkenes to linear alcohols was described. A (bcope)Pd(OTf)$_2$ complex (bcope) = bis (cyclooctyl)phosphinoethane, with substoichiometrically added halide anion was found to be a highly efficient homogeneous catalyst to selectively convert internal linear alkenes into predominantly linear alcohols under mild conditions (105 °C, 60 bar CO:H$_2$ = 1:1) [37].

A mixed ionic liquid [bmim][Cl,NTf$_2$] system was successfully used as a reaction medium for ruthenium-catalyzed hydroformylation of 1-hexene with carbon dioxide in the absence of toxic CO and any volatile organic solvents. Thus, from 20 mmol 1-hexene in [bmim][Cl,NTf$_2$] containing 0.1 mmol Ru$_3$(CO)$_{12}$ 82% heptanal was obtained at 160 °C under 40 bar CO$_2$ and 40 bar H$_2$ pressure in 10 h [38].

Efficient chemoselective hydroformylation of monosubstituted alkenes was observed at room temperature under atmospheric pressure of CO:H$_2$ = 1:1, without affecting functional groups such as disubstituted alkene moieties, aryl and alkenyl iodide moieties, and hydroxy and carboxy groups [39]. For example:





The hydride complexes IrH(CO)$_2$(XANTPHOS) and IrH$_3$(CO)(XANTPHOS), as well as the propionyl complex Ir(COEt)(CO)$_2$(XANTPHOS) were found to be modest catalysts for the hydroformylation of 1-hexene and styrene under mild conditions. Propionyl dihydride species IrH$_2$(COEt)(CO)(XANTPHOS) was detected by addition of parahydrogen to Ir(COEt)(CO)$_2$(XANTPHOS) [40].

(Diphosphine monosulfide)platinum(II) complexes (Ph$_2$CH$_2$P(S)Ph$_2$)Pt(CH$_3$(Cl)), (Ph$_2$CH$_2$CH$_2$P(S)Ph$_2$)-Pt(CH$_3$(Cl)), and (Ph$_2$CH$_2$CH$_2$CH$_2$P(S)Ph$_2$)Pt(CH$_3$(Cl)), were found to be good catalyst precursors for the hydroformylation of 1-octene at 80 °C and 50 bar CO:H$_2$ = 1:1 in the presence of SnCl$_2$ in methyl isobutyl ketone solution [41]. A xanthene-based chiral diphosphonite was applied in the Pt/Sn-catalyzed hydroformylation of styrene, 4-methylstyrene, vinyl acetate, and allyl acetate, by using a Pt/Sn ratio of 1:1. High ee of up to 80% were observed, along with good regioselectivities towards the branched aldehydes [42].

## 1.2. Heterogeneous systems

### 1.2.1. Supported metal catalysts

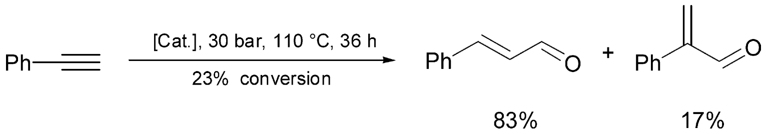
Hydroformylation of 1-hexene for oxygenate fuels via promoted cobalt/active carbon catalysts at low-pressure was investigated. Small amount of Pt, Pd and Ru, added as promoters led to a great improvement of catalytic activity. The best promotional effect was found for ruthenium [43].

Effect of addition of vanadium oxide to Rh/SiO$_2$ catalyst in hydroformylation of ethene and carbon monoxide hydrogenation was investigated. In the hydroformylation of ethene, the addition of vanadium oxide was found to enhance the hydroformylation activity and selectivity. It was suggested that the active site consists of rhodium metal and partially reduced VO$_x$ which is formed by the reduction of RhVO$_4$ [44]. Siliceous mesostructured cellular foams were employed as supports in developing the PPh$_3$–Rh/supported catalyst for propene hydroformylation in a fixed-bed reactor. The new catalyst shows high selectivity (*n*-butyraldehyde/isobutyraldehyde = 10.4), and excellent stability under mild conditions (10 bar, 120 °C) [45]. Heterogeneous chiral catalysts were prepared by modifying silica-supported rhodium with chiral phosphorus ligands. The chirally modified Rh/SiO$_2$ catalysts were found to exhibit high activity, regioselectivity, and enantioselectivity for the asymmetric hydroformylation of styrene and vinyl acetate. Up to 72% ee and 100% selectivity of branched aldehyde for the hydroformylation of vinyl acetate were obtained for (*R*)-BINAP-Rh/SiO$_2$ catalysts [46].

Rhodium nanoparticles were used as catalyst precursors for the solventless hydroformylation of 1-alkenes. Linear/branched selectivities up to 25 were achieved by addition of XANTPHOS to the catalyst system [47].

### 1.2.2. Supported complexes

The regioselective hydroformylation of terminal alkynes was reported using a heterogenized rhodium catalyst on mesoporous zirconium oxide at 110 °C and 30 bar CO:$H_2$: = 1:1 [48]. For example:

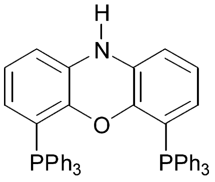


The effect of $H_3PW_{12}O_{40}$ and $P(OPh)_3$ on the activity and selectivity of MCM-41-supported rhodium(I) and rhodium(III) catalysts was investigated in the hydroformylation reaction of 1-octene and styrene. The heteropolyacid-impregnated catalyst was found to enhance the catalytic activity [49]. The addition of $P(OPh)_3$ increased the selectivity of the reaction towards the branched product [50].

The kinetics of hydroformylation–acetalization of 1-hexene using [Rh(COD)(4-picoline)$_2$][PF$_6$] immobilized on poly(4-vinylpyridine) as the catalyst in methanol was investigated. The catalytic activity proved to be non-linear in the rhodium total concentration [51]. Highly dispersed rhodium catalysts on solid supports were tested in olefin hydroformylation. Compared to other known heterogenized catalyst the highly dispersed catalyst was found to have a significantly higher activity [52]. Hydroformylation of internal octenes was investigated using an encapsulated rhodium catalyst made from [Rh(acac)(CO)$_2$], tris(3-pyridyl)phosphine and zinc(II) tetraphenylporphyrin by self-assembly. *Trans*-2-octene was hydroformylated at 25 °C and 20 bar CO:$H_2$ = 1:1 to give 87.8% 2-ethylheptanal and 9.4% 2-methyl-octanal [53].

A supported rhodium complex catalyst obtained by impregnation of $HRh(CO)(PPh_3)_3$ on a solid base hydrotalcite was found to be active in hydroformylation and aldol condensation. This catalyst was used for single-pot synthesis of C-8 aldol derivatives from propene under varied reaction parameters [54].

NIXANTPHOS (**12**) and its modified derivatives were immobilized on soluble and solid polymer supports, such as dendrimers, polyglycerol and polyurethanes. The new catalysts were tested in rhodium-catalyzed regioselective hydroformylation of 1-octene [55].



**12**

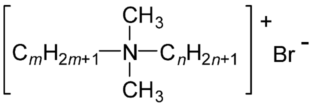
See also Ref. [18].

### 1.2.3. Biphasic systems

Styrene lattices were tested as phase-transfer agents in the aqueous-phase hydroformylation of 1-octene using $HRh(CO)(TPPTS)_3$ as the catalyst [56].

The water-soluble complex [HRu(CO)(CH$_3$CN)(TPPTS)$_3$] [BF$_4$] has been used as catalyst precursor for the aqueous biphasic hydroformylation of several olefins and their mixtures under moderate reaction conditions. The catalytic activity order found was: 1-hexene > allylbenzene > 2,3-dimethyl-1-butene > styrene > cyclohexene. It was found that the complex maintains its activity when the thiophene concentration is below 500 ppm [57].

Hydroformylation of long-chain internal olefins with water-soluble cobalt/phosphine complexes in a two-phase system was investigated. Best results, up to 85–90% aldehyde selectivities and 78% aldehyde yields, were obtained at 170 °C and 160–200 bar CO:$H_2$ = 1:1 in 16 h using TPPTS and $Ph_2P(CH_2)_3SO_3Li$ as the ligands [58]. The rhodium/TPPTS-catalyzed hydroformylation of higher olefins in organic/aqueous biphasic system in the presence of double long-chain cationic surfactants (**13**) was studied at 100 °C and 20 bar CO:$H_2$ = 1:1 pressure [59].



$$\left[ C_mH_{2m+1}-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{N}}-C_nH_{2n+1} \right]^+ Br^-$$

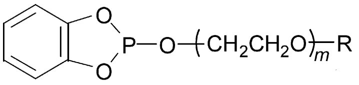
$m$ = 16, 20

$n$ = 2, 4, 8, 12, 16, 22

**13**

The rhodium-catalyzed hydroformylations of higher olefins in an aqueous/organic biphasic system in the presence of new surface-active phosphines (sodium salt of sulfonated $C_{12}H_{25}C_6H_4PPh_2$ and $C_8H_{17}C_6H_4PPh_2$) were investigated [60].

Thermoregulated poly(ethylene glycol) biphase system was used in the hydroformylation of *p*-isobutylstyrene catalyzed by a rhodium(**14**)-complex. Under the conditions of 50 bar CO:$H_2$ = 1:1, P/Rh molar ratio of 8, and 5 h reaction time at 120 °C, 99% conversion of *p*-isobutylstyrene, and 96% yield of aldehyde was achieved [61].



R = $C_8H_{17}$

$m$ = 12, 19, 44, 67

**14**

A new combination for biphasic rhodium-catalyzed hydroformylation of higher olefins was investigated. It was found that methylated cyclodextrins/tris(*m*-carboxyphenyl)phosphine trilithium salt couples are more efficient than the well-known methylated cyclodextrin/TPPTS systems in terms of activities and selectivities to perform the rhodium-catalyzed hydroformylation of higher olefins in an aqueous–organic system [62].

Catalysis with water-soluble rhodium complexes, RhCl(CO)(TPPMS)$_2$, RhCl(CO)(TPPDS)$_2$, RhCl(CO)(TPPTS)$_2$, in hydroformylation of 1-hexene, 2-pentene, 2,3-dimethyl-1-butene, cyclohexene and several mixtures of these olefins were studied under moderate reaction conditions. The linear and branched oxygenated products obtained at 50–150 °C, 14–68 bar CO:$H_2$ = 1:1 pressures in biphasic toluene/water media were found to be useful in naphtha upgrading [63].

Adsorptions at the liquid–liquid interface in the biphasic rhodium/TPPTS-catalyzed hydroformylation of olefins promoted by cyclodextrins were studied. It was found that the most important key partners involved in the hydroformylation reaction concentrate at the interface, thereby facilitating the reaction, a process which may be further facilitated upon complexation by cyclodextrins [64]. The potential of alkyl sulfonated diphosphine ligands associated with methylated alpha- and beta-cyclodextrin during the reaction of rhodium-catalyzed hydroformylation of 1-decene was studied. In all cases, the presence of cyclodextrins increased the conversion and the chemoselectivity whereas the linear to branched ratio of the aldehyde product decreased. The decrease in regioselectivity was attributed to the formation of low-coordinated phosphine species [65].

Hydroformylation of 1-hexene was studied in aqueous medium using $RhCl_3 \cdot xH_2O$ or HRh(CO)(TPPTS)$_3$ as the catalyst precursor [66]. Halogen-free ionic liquids, 1-alkyl-3-methyl-imidazolium *p*-toluenesulfonate were applied as the reaction media in the HRh(CO)(TPPTS)$_3$-catalyzed hydroformylation reaction of long-chain olefins. The results showed that the activity of the catalyst decreased with the increase of chain-length of olefins, and the activity was related with the chain-length of the alkyl group of the ionic liquids [67]. The rhodium/TPPTS-catalyzed hydroformylation of 1-octene was studied in microemulsion containing alkylpolyglycolether-type surfactant [68]. Hydroformylation of micro emulsified 1-dodecene and 1-tetradecene using sodium dodecyl sulfate or sodium dodecylbenzene sulfonate as detergents and Rh(acac)(CO)(TPPTS)$_3$ as the catalyst precursor was studied. At 100 °C and 20 bar CO:$H_2$ = 1:1 in aqueous butanol the corresponding aldehydes were obtained in 91 and 97.5% yield [69].

The rhodium-catalyzed hydroformylation of beta-isophorone was investigated under biphasic reaction conditions. At 60–120 °C and 100–180 bar CO:$H_2$ = 1:1 the hydroformylation of beta-isophorone afforded (3,3-dimethyl-5-oxo-cyclohexyl) acetaldehyde as the main product instead of the expected 4-formyl-3,5,5-trimethylcyclohexan-1-one [70] (see also Refs. [18,19]).

### *1.3. Coordination chemistry related to hydroformylation*

A DFT study on carbon monoxide insertion into cobalt–ethyl and cobalt–vinyl bonds of $EtCo(CO)_n(PH_3)_{4-n}$ and $CH_2{=}CHCo(CO)_n(PH_3)_{4-n}$, respectively was carried out. The computational results indicate that carbon monoxide insertion into an $sp^2$ carbon is easier than the carbon monoxide insertion into an $sp^3$ carbon from the view of kinetics except for the three-$PH_3$-ligand-substituted system. Transition states of all processes occur late on the potential energy surface and the transition states of vinyl migration occur later than ethyl migration [71].

The reaction of the *N*-heterocyclic carbene-containing compounds Co(IMes)(CO)$_3$(COMe) and Co(IMes)(CO)$_3$(COEt) with dihydrogen were shown to form the cobalt hydride compound HCo(IMes)(CO)$_3$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) [72].

New mechanistic insights were obtained in the rhodium(I)/aminophosphine-catalyzed styrene hydroformylation by using $D_2O$ as deuterium-labeling agent. H/D exchange of the rhodium–hydride complex, and the reversibility of the styrene coordination has been established. Based on the product compositions protonolysis of the rhodium–acyl intermediate and a bimolecular reaction involving the rhodium–acyl and rhodium–hydride intermediates as the aldehyde forming step were excluded [73].

The hydroformylation of cyclooctene was studied using $Rh_4(CO)_{12}$ as precursor in *n*-hexane solvent in the temperature range: 20–35 °C and the pressure range: 40–80 bar, using quantitative in situ infrared spectroscopy. The observed linear-quadratic kinetics of the reaction was regarded as experimental evidence for a significant homometallic catalytic binuclear elimination [74].

Results of theoretical investigation of the rhodium(I)-catalyzed hydroformylation of 1-phenyl-1-(4-pyridyl)ethene using a nonlocal density functional method (B3LYP) were published. The reaction was found to be strongly exothermic by >90 kJ/mol, and the rate limiting step to be $H_2$ oxidative addition [75] (see also Ref. [40]).

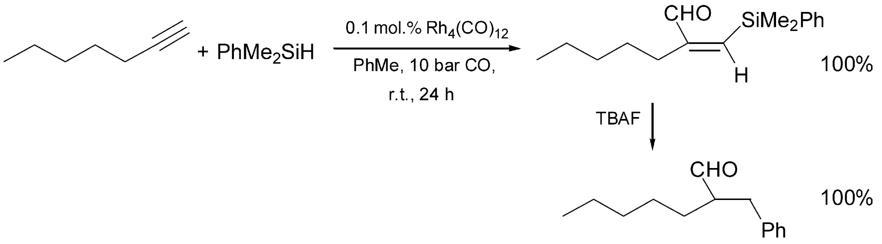
## 2. Hydroformylation related reactions of CO

### *2.1. Silylformylation and silylcarbocyclization*

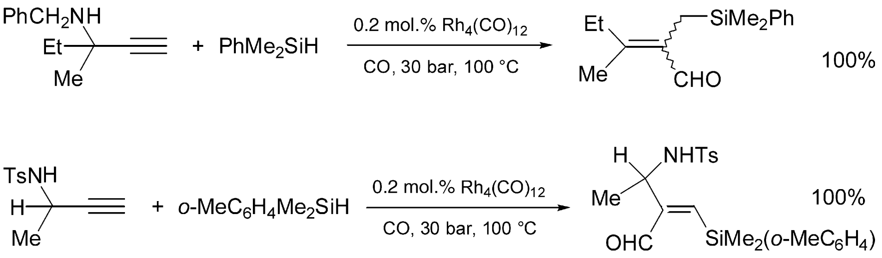
Cationic complexes of dirhodium(II) [$Rh_2(OAc)_2(MeCN)$][$BF_4$]$_2$, [$Rh_2(OAc)_3(Naft)$](OAc), and [$Rh_2(MeCN)_2(Naft)_4$][$BF_4$]$_4$ (Naft = 1,8-naphthyridine) were found to be selective catalysts of 1-hexyne silylformylation with $Me_2PhSiH$ at room temperature and 10 bar CO in dichloromethane solution. Only the *Z*-isomer of the silylformylated product was observed with 94, 93, and 99% selectivities, respectively [76].

Bimetallic synergism in alkyne silylformylation catalyzed by a cobalt–rhodium mixed-metal cluster was elucidated with density functional calculations. The catalytic cycle consists of oxidative addition of hydrosilane, alkyne insertion, CO insertion, and reductive elimination. While major bond-forming events take place only at the rhodium center, the cobalt also plays an important role; it fixes the metal cluster on the organic substrate, keeps the hydride ligand temporarily on the metal center, and suppresses hydrosilylation, which would otherwise be preferred over silylformylation [77].

Polyfunctionalized aldehydes and dihydropyrans were prepared from easily available functionalized 1-alkynes through a two-step silylformylation/aryl migration sequence. The silylformylation process was performed under mild experimental conditions and affords the corresponding beta-silylalkenal in high yields [78]. For example:



The $Rh_4(CO)_{12}$-catalyzed silylformylation of propargyl amides with aryldimethylsilanes was investigated. Depending on the substituents selective product formations were observed [79]. For example:



## 2.2. *Hydroxycarbonylation, hydroalkoxycarbonylation and alkoxycarbonylation*

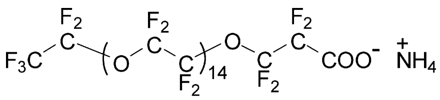
A palladium–salicylborate-catalyzed efficient and regioselective methoxycarbonylation of terminal alkyl and aryl olefins was described. The regioselectivity, in favor of the linear ester, was found to be up to quantitative in the case of styrenes [80].

The hydroxycarbonylation of 1-hexene to heptanoic acid and the water-gas-shift reaction catalyzed by the rhodium(I) complexes, $[Rh(COD)(amine)_2][PF_6]$ (amine = 4-picoline, 3-picoline, 2-picoline, pyridine, 3,5-lutidine or 2,6-lutidine) immobilized on poly(4-vinylpyridine) in contact with water under carbon monoxide was studied [81].

Hydroalkoxycarbonylation of ethene and alpha-olefins in the presence of several types of palladium–phosphine complexes was studied. High activity in the hydroalkoxycarbonylation of ethene and high regioselectivities (83–100%) in the hydroalkoxycarbonylation of alpha-olefins with respect to linear products were found [82]. Reactivities of alcohols in the $PdCl_2(PPh_3)_2$-catalyzed hydroalkoxycarbonylation of cyclohexene was investigated. The alcohol reactivity was found to be: *n*-BuOH > *n*-PrOH > *iso*-BuOH > MeOH > EtOH > $^c$HxOH > *iso*-PrOH [83].

All the intermediates in the “carboalkoxy” pathway, and their interconversions giving complete catalytic cycles, for palladium–diphosphine-catalyzed hydroalkoxycarbonylation of alkenes have been demonstrated using $^{31}P$ and $^{13}C$ NMR spectroscopy. The propagation and the termination steps of the “hydride” cycles and the crossover between the hydride and carboalkoxy cycles have also been demonstrated [84]. Palladium(II) complexes with *o*-aryl substituted 1,1′-bis(phosphino) ferrocenes were found to be selective catalysts of moderate activity for methoxycarbonylation of ethene [85].

High selectivity in acids (up to 90%) was obtained in hydrocarboxylation of 1-octene in supercritical carbon dioxide using a Pd/P(4-$CF_3$-$C_6H_4$)$_3$ catalyst system and a perfluorinated surfactant **15** [86].



**15**

The kinetics of cyclohexene hydrocarbomethylation catalyzed by the $Pd(PPh_3)_2Cl_2/PPh_3/p\text{-}TsOH$ system was reported. Based on the observed kinetics a mechanism involving cationic hydride complexes as intermediates was suggested [87]. The electronic effect of diphosphines on the regioselectivity of the palladium-catalyzed hydroesterification of styrene was studied. It was found that in the presence of electron-poor phosphines branched esters are produced and high activities of the catalytic systems were observed [88].

Hydroalkoxycarbonylation of styrene using palladium-based catalysts was studied in quaternary ammonium salts as reaction media. Under the reaction conditions applied (110 °C and 50 bar CO), the catalyst-containing phase can be reused several times without a significant decrease in catalytic activity [89]. Imidazolium-based ionic liquids with $[PF_6]^-$, $[BF_4]^-$, and $[GaCl_4]^-$ counter ions were synthesized and used in hydroethoxycarbonylation of styrene. Moderate to high regioselectivities towards branched esters were obtained with preformed $PdCl_2(PPh_3)_2$ catalyst [90].

The fluorous palladium(II) complex $[Pd(OAc)_2\{P(C_6H_4\text{-}p\text{-}SiMe_2CH_2CH_2C_6F_{13})_3\}_2]$ was applied as the catalyst precursor in the catalytic methoxycarbonylation of styrene in an $MeOH/CF_3Ph$ = 1/1 (v/v) mixture, and its activity was compared to that of $[Pd(OAc)_2(PPh_3)_2]$. The fluorous complex showed a lower activity but a significantly higher selectivity towards the branched product [91].

The palladium-catalyzed asymmetric methoxycarbonylation of styrene in the presence of chiral ferrocenyl phosphine ligands was investigated. In the best case 86% enantiomer excess was achieved, however the regioselectivity of the reaction was found to be in favor of the undesired linear ester [92].

The omega-hydroxyalkenes 3-buten-1-ol, 3-buten-1-methyl-1-ol, and 4-penten-1-ol were subjected to hydroxycarbonylation conditions in water in the presence of $PdCl_2(PhCN)_2$ and 4–8 equiv. of water-soluble TPPTS or N3P (N3P = *N*-bis(*N*′,*N*′-diethyl-2-aminoethyl)-4-aminomethylphenyl-diphenylphosphine). Under conditions of high conversion, selectivities for aldehyde ranging from 65 to 98% were observed [93]. The regioselectivity in aqueous palladium-catalyzed hydroxycarbonylation of styrene was investigated using TPPTS and N3P as ligands. The factor giving the highest changes in regioselectivity in the TPPTS system was found to be the temperature. In the N3P case, only a minor variation in the *n*/iso ratio as a function of temperature was observed. Two palladium hydride intermediates, a palladium eta3-benzylic complex and both the branched and linear palladium–acyl complexes were identified in the high pressure NMR experiments [94]. The palladium-catalyzed aqueous hydrocarboxylation reaction of styrene, 1-octene, 3-buten-1-ol, and 4-pentenoic acid was studied in acidic solutions. The catalyst employing N3P as ligand was found to show an inverted regioselectivity compared to the TPPTS system [95].

Palladium complexes of [1,2-phenylenebis(methylen)] bis[di(*tert*-butyl)phosphine] were found to catalyze the methoxycarbonylation of vinyl acetate in the presence of methanesulfonic acid. High selectivities to ester products were obtained if free phosphine ligand is in excess over the amount of added acid [96].

The palladium-catalyzed selective alkoxycarbonylation of enamide was studied using *N*-vinylphthalimide as the model substrate. The effects of phosphine ligands and other reaction parameters were investigated [97].

Palladium complexes of 2-pyridyldiphenylphosphine anchored on polystyrene, polymethylmethacrylate, and styrene-methylmethacrylate copolymer were found to form highly active heterogeneous catalysts for the alkoxycarbonylation of terminal alkynes with activities approaching those obtained under homogeneous conditions [98].

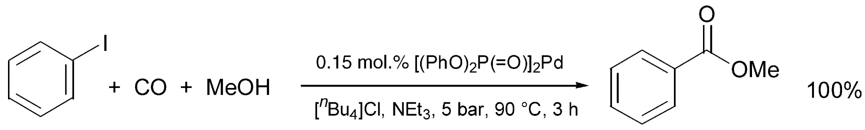
The methoxycarbonylation of propylene oxide to methyl beta-hydroxybutyrate catalyzed by dicobaltoctacarbonyl and 3-hydroxypyridine in methanol system were studied, and the effects of reaction parameters were investigated. At 80 °C and 60 bar CO pressure using a 2:1 = 3-hydroxypyridine:$Co_2(CO)_8$ molar ratio 80.4% conversion of propylene oxide and 74.9% yield of methyl beta-hydroxybutyrate was observed [99].

Phosphine-free palladium catalysts were found to be active in bromide-containing molten salts such as tetrabutylammonium bromide and [bmim]Br for hydrocarbonylation of 1-phenylethanol [100]. $PdCl_2$(2-(beta-diphenylphosphino) ethylpyridine) was found to be effective in the promotion of the alkoxycarbonylation of diols into cyclic carbonates or other valuable carbonyl products [101].

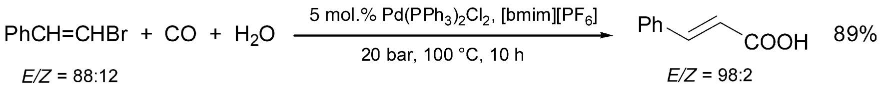
An operationally simple hydroxycarbonylation of aryl and vinyl triflates to the corresponding carboxylic acids with palladium-mediated microwave system was described. Thus, heating aryl or vinyl triflates with 10 mol.% palladium(II) acetate/dppf catalyst and 0.5 equiv. $Mo(CO)_6$ as a solid carbon monoxide source at 150 °C for 20 min give the corresponding acids in up to 97% yield [102]. Microwave-promoted 0.1–0.1 mol.% palladium salts-catalyzed hydroxycarbonylation of aryl iodides in water using gaseous carbon monoxide and pre-pressurized reaction vessels was reported [103]. The catalytic activity of palladium colloids in methoxycarbonylation of iodobenzene was investigated [104].

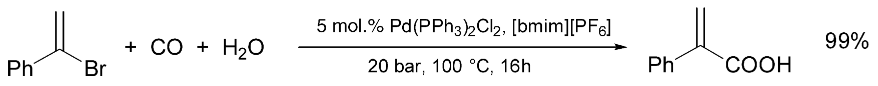
The palladium(II) complexes, $PdCl_2(COD)$, $PdCl_2[P(OPh)_3]_2$, $[bmim]_2[PdCl_4]$, and $[bmpy]_2[PdCl_4]$ were found to be active catalysts for the methoxycarbonylation of iodobenzene in ionic liquid media. The best results (76–100% yield) were obtained in pyridinium salts [bmpy]X (X = Cl, Br, $BF_4$, $PF_6$) [105].

New phosphinite and phosphonite complexes were found to be efficient catalysts for the methoxycarbonylation of iodobenzene [106]. For example:



Palladium-catalyzed hydroxycarbonylation of vinyl bromides in an ionic liquid to alpha,beta-unsaturated carboxylic acids was reported [107]. For example:





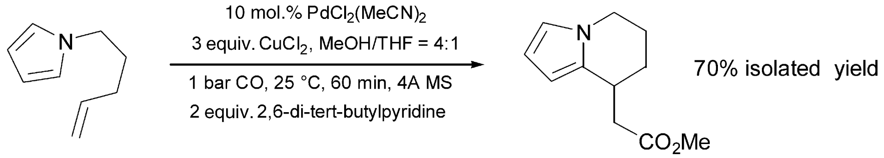
A general palladium-catalyzed alkoxycarbonylation of aryl and heteroaryl bromides to ester, amide or acid derivatives was developed using the bulky monodentate phosphine di-1-adamantylbutylphosphine as catalyst-modifying ligand. Studies of the butoxycarbonylation of 4-bromoanisole, 3-bromopyridine, and 4-bromoacetophenone revealed the advantages of di-1-adamantylbutylphosphine compared to other ligands. In the presence of this catalyst system various bromoarenes provided at 115 °C and 20 bar CO the corresponding benzoic acid derivatives in excellent yields at low (0.5 mol.% $Pd(OAc)_2$ + 1.5 mol.% di-1-adamantylbutylphosphine) catalyst loading [108].

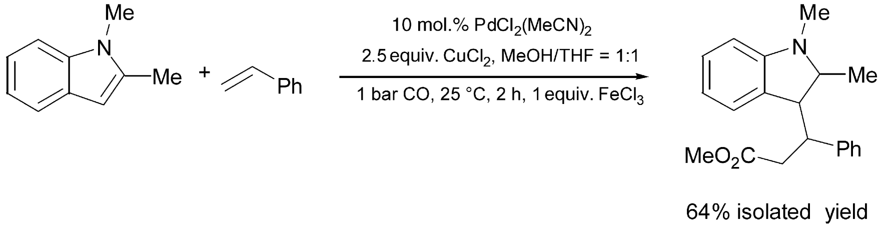
Palladium-catalyzed carboalkoxylation of 1,2-dibromo-3,3,3-trifluoropropane with *tert*-butyl alcohol to provide *tert*-butyl trifluoromethylmethacrylate was improved by the addition of $Li_2CO_3$. It was found that $Li_2CO_3$ not only accelerated the reaction drastically but also suppressed the further reaction of the methacrylate and alcohol completely [109]. The palladium-catalyzed hydroxycarbonylation of aryl and vinyl bromides in the presence of acetic anhydride and lithium formate as a carbon monoxide source was developed. The combination of palladium(II) acetate with 1,1′-bis(diphenylphosphino)ferrocene (dppf) was found to be an efficient catalytic system when the reaction is carried out at 120 °C [110].

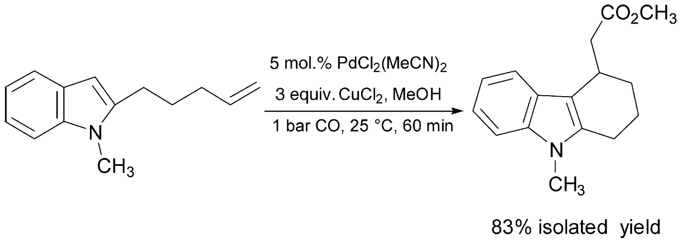
Highly dispersed supported ionic liquid-phase palladium catalyst was prepared and its catalytic performances for carbonylation of aryl halides were investigated. The supported ionic liquid-phase palladium catalyst exhibit higher activity in the carbonylation of aryl halides compared with the corresponding organic–ionic liquid biphasic system. Under optimum reaction conditions: 140 °C, 40 bar CO, mol(PhI):mol(Pd) = 10,528:1, the turnover frequency of 4926 $h^{-1}$ was achieved for ethyl benzoate with 99.3% conversion and 99% selectivity [111].

Aryl carboxylic esters were synthesized by palladium-catalyzed carbonylation of aryl *p*-fluorobenzenesulfonates or -tosylates. Isolated yields of up to 90% were obtained [112].

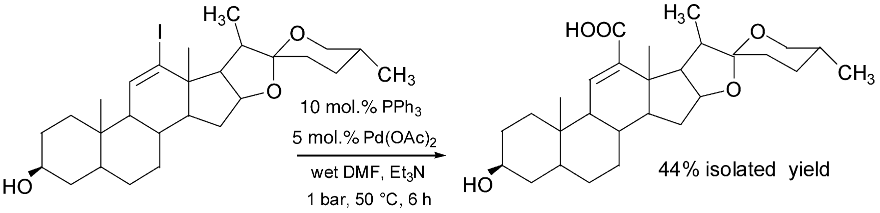
A mild and effective palladium(II)-catalyzed, copper(II)-mediated protocol for the arylation/carboalkoxylation of unactivated olefins with indoles was developed [113]. For example:

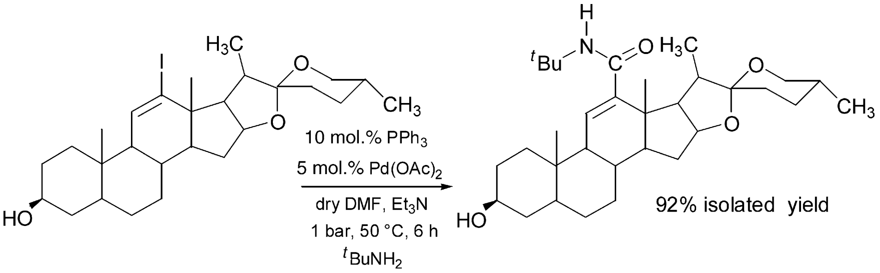






12-Carboxamido- and 12-carboxyl-11-spirostenes were synthesized from the corresponding 12-iodo-11-ene derivative in palladium-catalyzed carbonylation reactions under mild reaction conditions [114]. For example:

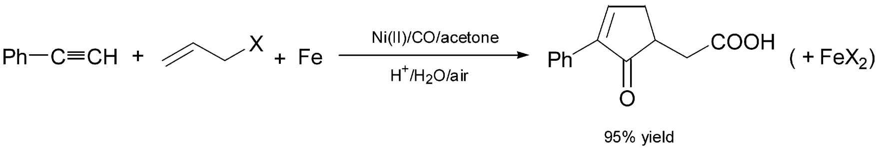


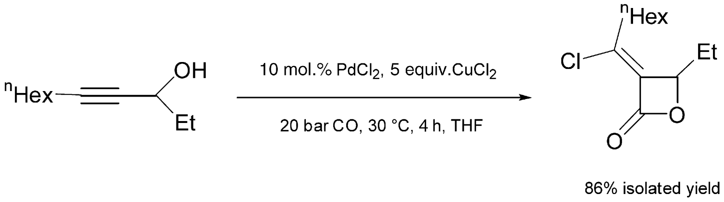


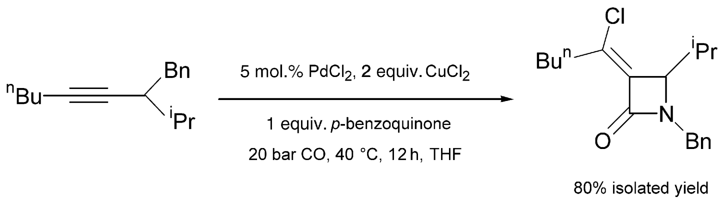
See also Ref. [124].

### 2.3. Cyclocarbonylation

Recyclable selective palladium-catalyzed synthesis of five-, six- or seven-membered ring lactones and lactams were reported by cyclocarbonylation of 2-allylphenols and anilines, 2-vinylphenols, and 2-aminostyrenes in ionic liquids. The reaction affords high yields of lactones or lactams with good or excellent selectivity for one isomer [115].



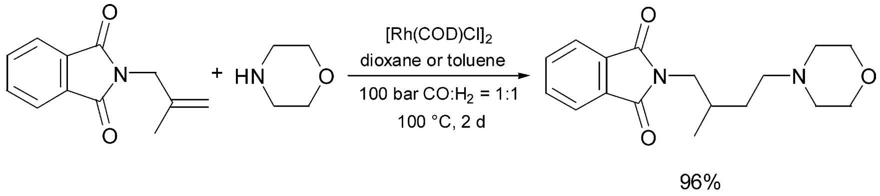


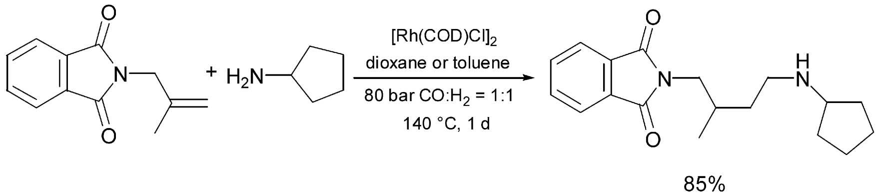


See also Ref. [127].

### 2.4. Aminocarbonylation, amidocarbonylation, and hydroaminomethylation

Polyamines, structurally related to putrescines and spermidines, were obtained via rhodium-catalyzed hydroaminomethylation of methallylphthalimide with primary or secondary amines [116]. For example:



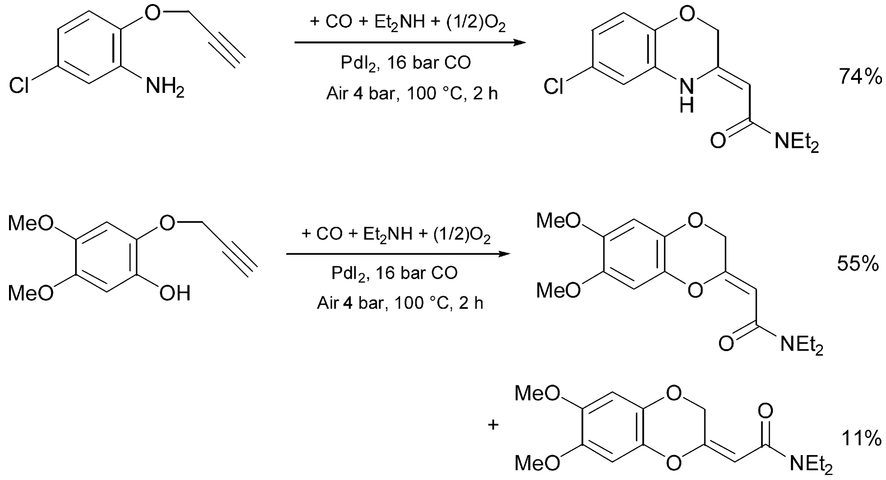


Phenoxaphosphino-modified XANTPHOS-type ligands in the rhodium-catalyzed hydroaminomethylation of internal olefins were found to give linear amines. Hydroaminomethylation and each of its individual steps were monitored by high-pressure infrared spectroscopy. The results suggest that hydroaminomethylation take place by a sequential isomerization/hydroformylation/amination/hydrogenation pathway [117].

The hydroaminomethylation of long-chain alkenes with secondary amines in aqueous/organic two-phase system catalyzed by rhodium catalyst precursor and water-soluble diphosphine ligand BISBIS was investigated. The use of BISBIS gave higher activity and higher regioselectivity for linear amine than the monophosphine ligand TPPTS. The ratio of linear to branched amine was found to be up to 83 [118]. The hydroaminomethylation of long-chain alkenes with secondary amines was performed efficiently in ionic liquids 1-*n*-alkyl-3-methylimidazolium tosylates (alkyl = *n*-butyl, octyl, dodecyl, cetyl) with Rh–BISBIS complex as catalyst [119].

Regiospecific construction of 2-substituted acrylamides was achieved by palladium-catalyzed aminocarbonylation of alkynes in the ionic liquid [bmim][Tf$_2$N] without any acid additive under relatively mild conditions. The ionic liquid was used as the reaction medium and also acted as a promoter [120].

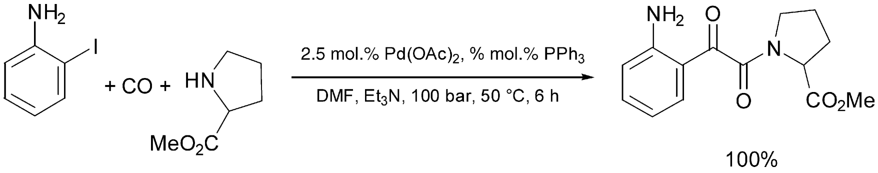
A new synthesis of 2,3-dihydrobenzo[1,4]dioxine and 3,4-dihydro-2*H*-benzo[1,4]oxazine derivatives by tandem palladium-catalyzed oxidative aminocarbonylation-cyclization of 2-prop-2-ynyloxyphenols and 2-prop-2-ynyloxyanilins were published [121]. For example:



A polymer-supported catalytic system was assembled from Pd(dba)$_2$ and a polymer-bound diphosphine chelate, prepared via solid-phase synthesis from serinol. The system was found to convert aryl bromides into carboxamides in a reaction with carbon monoxide and aliphatic or aromatic amines [122].

A microwave-enhanced novel palladium-catalyzed and Mo(CO)$_6$ promoted aminocarbonylation protocol was developed for rapid generation of primary aromatic amides from aryl bromides and iodides in dioxane solution. Employing controlled microwave heating, hydroxylamine was first reduced in situ to ammonia, which thereafter reacted with carbon monoxide and the aryl halide substrate, delivering the benzamide product in less than 20 min [123]. Using both primary and secondary amines in water, the method was applied for aminocarbonylation of aryl iodides, aryl bromides, and aryl chlorides [124].

The direct transformation of aryl bromides into the corresponding amides via palladium-catalyzed aminocarbonylation at atmospheric pressure was reported [125]. Methyl prolinate and benzyl prolinate were used as secondary amine nucleophiles in palladium-catalyzed aminocarbonylation of iodo-aromatics and iodo-alkenes. A mixture of 2-oxo-carboxamide and carboxamide type derivatives or pure carboxamides were obtained at 50 °C and 1–40 bar CO pressure [126]. Keto-carboxamides were prepared by palladium-catalyzed carbonylation of 2-iodoaniline in the presence of various primary and secondary amines [127]. For example:



The palladium-catalyzed amidocarbonylation reaction was studied in recyclable ionic liquids [128] and by using HZSM-5-supported palladium catalyst [129] (see also Ref. [114]).

## 3. Reviews

(1) Hydroformylation. A review on the most important example of the industrial application of homogeneous catalysis used to produce more then 10 million metric tonnes annually, with 90 references from the scientific and patent literature [130].

(2) Selected problems of hydroformylation such as the influence of phosphorus ligands on the selectivity of hydroformylation of monoolefins, dienes and unsaturated alcohols, and the reactivity of rhodium catalysts supported on $Al_2O_3$–$ZrO_2$ and on $SiO_2$, were reviewed based on studies conducted at the Faculty of Chemistry University of Wroclaw with 30 references [131].

(3) The latest developments in supported ionic liquid-phase systems for hydroformylation and carbonylation catalysis and separation technology were surveyed. A review with 65 references [132].

(4) Recent developments in the design of rhodium-based catalysts for hydroformylation in supercritical carbon dioxide. A review with 75 references [133].

(5) Recent advances in the synthesis of heterocycles through hydrosilylation, silylformylation, silylcarbocyclization and cyclohydrocarbonylation were reviewed with 102 references [134].

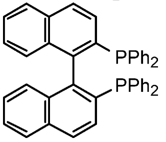
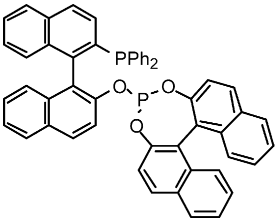
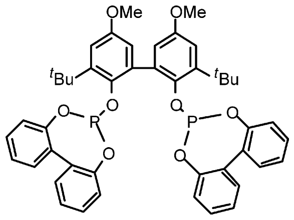
(6) Multiphase systems for the recycling of alkoxycarbonylation catalysts. A review evaluating the various multiphase systems that have been developed for catalyst recycling in context of alkoxycarbonylation of alkenes and alkynes. A review with 69 references [135].

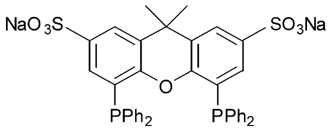
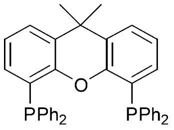
(7) New developments in the area of oxime palladacycles-catalyzed alkoxycarbonylation reactions. A review from a mechanistic and synthetic point of view with 96 references [136].

## Acknowledgment

The author thanks the Hungarian Science Fund for support under Grant no. OTKA T037817.

## Appendix A. List of abbreviations

| | |
|---|---|
| Ac | acetyl |
| acac | acetylacetonate |
| Ar | aryl |
| BINAP | 2,2′-bis(diphenylphosphano)-1,1′-binaphthyl<br> |
| BINAPHOS |  |
| BIPHEPHOS |  |
| BISBIS | sodium salt of sulfonated 2,2′-bis(diphenylphosphinomethyl)-1,1′-biphenyl |
| [bmim]$^+$ | 1-butyl-3-methylimidazolium cation |
| [bmpy] | 1-butyl-4-methylpyridinium cation |
| Bu | butyl |
| $^i$Bu | isobutyl |
| COD | 1,5-cyclooctadiene |
| Cp | cyclopentadienyl |
| Cp* | pentamethylcyclopentadienyl |
| dba | dibenzylideneacetone |

| | |
|---|---|
| DMF | *N,N*-dimethylformamide |
| DFT | density functional theory |
| dppb | $Ph_2PCH_2CH_2CH_2CH_2PPh_2$ |
| dppe | $Ph_2PCH_2CH_2PPh_2$ |
| dppf | $1,1'$-bis(diphenylphosphinol)ferrocene |
| ee | enantiomeric excess |
| Et | ethyl |
| FTIR | Fourier transform infrared |
| $^c$Hx | cyclohexyl |
| IMes | 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene |
| Me | methyl |
| Naft | 1,8-naphthyridine |
| NBD | norbornadiene |
| N3P | $N$-bis($N'$,$N'$-diethyl-2-aminoethyl)-4-aminomethylphenyl-diphenylphosphine |
| Ph | phenyl |
| $^i$Pr | isopropyl |
| py | pyridine |
| sc | supercritical |
| sulfoXANTPHOS |  |
| TBAF | tetrabutylammonium fluoride |
| THF | tetrahydrofuran |
| Tf | triflate (trifluoroacetyl) |
| TMS | trimethylsilyl |
| TOF | turnover frequency (mol product/(mol catalyst time)) |
| TON | turnover number (mol product/mol catalyst) |
| 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 | [48] |
| V | [44] |
| Mo | [102,123,124] |
| W | [39] |
| Fe | [85] |
| Ru | [38,43,57] |
| Co | [1,43,58,71,72,77,99,130] |
| Rh | [2–36,39,44–56,59–70,73–79,81,116–119,130,131] |
| Ir | [40] |
| Ni | [12] |
| Pd | [37,80,82–98,100–115,120–129,136] |
| Pt | [41,42] |
| Cu | [89,113] |
| Sn | [41,42] |

## References

[1] R.J. Klingler, M.J. Chen, J.W. Rathke, K.W. Kramarz, Organometallics 26 (2007) 352.

[2] S. Cossu, P. Peluso, E. Alberico, M. Marchetti, Tetrahedron Lett. 47 (2006) 2569.

[3] O. Artyushin, I. Odinets, E. Goryunov, I. Fedyanin, K. Lyssenko, T. Mastryukova, G.-V. Röschenthaler, T. Kégl, G. Keglevich, L. Kollár, J. Organomet. Chem. 691 (2006) 5547.

[4] J.J. Carbo, A. Lledos, D. Vogt, C. Bo, Chem. Eur. J. 12 (2006) 1457.

[5] J. Andrieu, J.M. Camus, P. Richard, R. Poli, L. Gonsalvi, F. Vizza, M. Peruzzini, Eur. J. Inorg. Chem. (2006) 51.

[6] Y.H. Yan, X.W. Zhang, X.M. Zhang, J. Am. Chem. Soc. 128 (2006) 16058.

[7] Y. Yan, X.M. Zhang, J. Am. Chem. Soc. 128 (2006) 7198.

[8] B.M. Fang, J.H. Xie, Z.T. Zhou, Q. Zhang, Y.Q. Tu, Q.L. Zhou, Chem. J. Chin. Univ. Chin. 27 (2006) 1894.

[9] G. Mora, S. van Zutphen, C. Thoumazet, X.F. Le Goff, L. Ricard, H. Grutzmacher, P. Le Floch, Organometallics 25 (2006) 5528.

[10] E.I. Tolis, K.A. Vallianatou, F.J. Andreadaki, I.D. Kostas, Appl. Organomet. Chem. 20 (2006) 335.

[11] M.L. Clarke, G.L. Roff, Chem. Eur. J. 12 (2006) 7978.

[12] L. Garcia, C. Claver, M. Dieguez, A.M. Masdeu-Bulto, Chem. Commun. (2006) 191.

[13] P. Linnepe, A.M. Schmidt, P. Eilbracht, Org. Biomol. Chem. 4 (2006) 302.

[14] A.M. Kleman, M.A. Abraham, Ind. Eng. Chem. Res. 45 (2006) 1324.

[15] P. Nanayakkara, H. Alper, Adv. Synth. Catal. 248 (2006) 545.

[16] M.G. Pedros, A.M. Masdeu-Bulto, J. Bayardon, D. Sinou, Catal. Lett. 107 (2006) 205.

[17] M. Gimenez-Pedros, A. Aghmiz, N. Ruiz, A.M. Masdeu-Bulto, Eur. J. Inorg. Chem. (2006) 1067.

[18] S. Paganelli, A. Ciappa, M. Marchetti, A. Scrivanti, U. Matteoli, J. Mol. Catal. A: Chem. 247 (2006) 138.

[19] J. Tijani, B. El Ali, Appl. Catal. A: Gen. 303 (2006) 158.

[20] E.A. Karakhanov, Y.S. Kardasheva, E.A. Runova, D.A. Sakharov, M.V. Terenina, Petrol. Chem. 46 (2006) 264.

[21] R. Abu-Reziq, H. Alper, D.S. Wang, M.L. Post, J. Am. Chem. Soc. 128 (2006) 5279.

[22] R. Abdallah, M.A.J. Breuzard, M.C. Bonnet, M. Lemaire, J. Mol. Catal. A: Chem. 249 (2006) 218.

[23] R.C. Nelson, C.R. Landis, Chim. OGGI Chem. Today 24 (Suppl. S) (2006) 36.

[24] X.L. Luo, D.Y. Tang, M. Li, J. Mol. Struct. Theochem. 763 (2006) 75.

[25] M.R. Axet, S. Castillon, C. Claver, Inorg. Chim. Acta 359 (2006) 2973.

[26] H. Jin, B. Subramaniam, A. Ghosh, J. Tunge, AIChE J. 52 (2006) 2575.

[27] J.C. Zhang, H.B. Wang, H.T. Liu, W.L. Cao, J. Mol. Catal. A: Chem. 260 (2006) 95.

[28] J.G. da Silva, H.J.V. Barros, E.N. dos Santos, E.V. Gusevskaya, Appl. Catal. A: Gen. 309 (2006) 169.

[29] E. Petricci, A. Mann, A. Schoenfelder, A. Rota, M. Taddei, Org. Lett. 8 (2006) 3725.

[30] A.C.J. Koeken, M.C.A. van Vliet, L.J.P. van den Broeke, B.J. Deelman, J.T.F. Keurentjes, Adv. Synth. Catal. 348 (2006) 1553.

[31] D. Semeril, C. Jeunesse, D. Matt, L. Troupet, Angew. Chem. Int. Ed. 45 (2006) 5810.

[32] E. Fuchs, M. Keller, B. Breit, Chem. Eur. J. 12 (2006) 6930.

[33] K. Nakano, R. Tanaka, K. Nozaki, Helv. Chim. Acta 89 (2006) 1681.

[34] R. Lazzaroni, S. Rocchiccioli, A. Iuliano, L. Cipolla, J. Organomet. Chem. 691 (2006) 4054.

[35] A.T. Axtell, J. Klosin, K.A. Abboud, Organometallics 25 (2006) 5003.

[36] B.M. Fan, J.H. Xie, Z.T. Zhou, Q. Zhang, Y.Q. Tu, Q.L. Zhou, Chin. J. Chin. Univ. Chin. 27 (2006) 1894.

[37] D. Kónya, K.Q.A. Lenero, E. Drent, Organometallics 25 (2006) 3166.

[38] K. Tominaga, Catal. Today 115 (2006) 70.

[39] M. Yamane, N. Yukimura, H. Ishiai, K. Narasaka, Chem. Lett. 35 (2006) 540.

[40] D.J. Fox, S.B. Duckett, C. Flaschenriem, W.W. Brennessel, J. Schneider, A. Gunay, R. Eisenberg, Inorg. Chem. 45 (2006) 7197.

[41] A. Lofu, P. Mastrorilli, C.F. Nobile, G.P. Suranna, P. Frediani, J. Iggo, Eur. J. Inorg. Chem. (2006) 2268.
[42] R. van Duren, L.L.J.M. Cornelissen, J.I. Van der Vlugt, J.P.L. Huijbers, A.M. Mils, A.L. Spek, C. Muller, D. Vogt, Helv. Chim. Acta 89 (2006) 1547.
[43] Y. Zhang, M. Shinoda, Y. Shiki, N. Tsubaki, Fuel 85 (2006) 1194.
[44] T. Yamagishi, I. Furikado, S. Ito, T. Miyao, S. Naito, K. Tomishige, K. Kunimori, J. Mol. Catal. A: Chem. 244 (2006) 201.
[45] L. Yan, Y.J. Ding, H.J. Zhu, H.M. Yin, G.P. Jiao, D.Y. Zhao, L.W. Lin, Chin. J. Catal. 27 (2006) 1.
[46] D.F. Han, X.H. Li, H.D. Zhang, Z.M. Liu, J. Li, C. Li, J. Catal. 243 (2006) 318.
[47] A.J. Bruss, M.A. Gelesky, G. Machado, J. Dupont, J. Mol. Catal. A: Chem. 252 (2006) 212.
[48] F. Goettmann, P. Le Floch, C. Sanchez, Chem. Commun. (2006) 180.
[49] B. El Ali, J. Tijani, M. Fettouchi, J. Mol. Catal. A: Chem. 250 (2006) 153.
[50] B. El Ali, J. Tijani, M. Fettouchi, Appl. Catal. A: Gen. 303 (2006) 213.
[51] F. Hung-Low, G.C. Uzcategui, J. Alvarez, M.C. Ortega, A.J. Pardey, C. Longo, React. Kinet. Catal. Lett. 88 (2006) 143.
[52] N.S. Pagar, R.M. Deshpande, R.V. Chaudhari, Catal. Lett. 110 (2006) 129.
[53] M. Kuil, T. Soltner, P.W.N.M. van Leeuwen, J.N.H. Reek, J. Am. Chem. Soc. 128 (2006) 11344.
[54] V.K. Shrivastava, S.K. Sharma, R.S. Shukla, R.V. Jasra, Catal. Commun. 7 (2006) 879.
[55] S. Ricken, P.W. Osinski, P. Eilbracht, R. Haag, J. Mol. Catal. A: Chem. 257 (2006) 78.
[56] K. Kunna, C. Muller, J. Loos, D. Vogt, Angew. Chem. Int. Ed. 45 (2006) 7289.
[57] P.J. Baricelli, K. Segovia, E. Lujano, M. Modrono-Alonso, F. Lopez-Linares, R.A. Sanchez-Delgado, J. Mol. Catal. A: Chem. 252 (2006) 70.
[58] M. Kant, A. Martin, G. Giuffrida, S. Rosano, Chem. Eng. Technol. 78 (2006) 913.
[59] H.Y. Fu, M. Li, H. Chen, X.J. Li, J. Mol. Catal. A: Chem. 259 (2006) 156.
[60] H.Y. Fu, Y. Guo, Q. Lin, H. Chen, X.J. Li, Chin. J. Catal. 27 (2006) 1053.
[61] C.L. Feng, Y.H. Wang, Y.J. Jiang, Y.C. Yang, F.L. Fu, Z.L. Jin, J. Mol. Catal. A: Chem. 248 (2006) 159.
[62] S. Tilloy, E. Genin, F. Hapiot, D. Landy, S. Fourmentin, J.P. Genet, V. Michelet, E. Monflier, Adv. Synth. Catal. 348 (2006) 1547.
[63] T. Suarez, B. Fontal, G. Leon, M. Reyes, F. Bellandi, R.R. Contreras, P. Cancines, Trans. Met. Chem. 31 (2006) 974.
[64] N. Sieffert, G. Wipff, J. Phys. Chem. B 110 (2006) 4125.
[65] S. Tilloy, G. Crowyn, E. Monflier, P.W.N.M. van Leeuwen, J.N.H. Reek, New J. Chem. 30 (2006) 377.
[66] W.J. Tic, Przem. Chem. 85 (2006) 767.
[67] Q. Lin, H.Y. Fu, F. Xue, M.L. Yuan, H. Chen, X.J. Li, Acta Phys. Chim. Sinica 22 (2006) 465.
[68] H.H.Y. Unveren, R. Schomacker, Catal. Lett. 110 (2006) 195.
[69] W.J. Tic, Przem. Chem. 85 (2006) 427.
[70] S. Paganelli, F. Battois, M. Marchetti, R. Lazzaroni, R. Settambolo, S. Rocchiccioli, J. Mol. Catal. A: Chem. 246 (2006) 195.
[71] X.L. Luo, D.Y. Tang, L. Ming, J. Mol. Catal. A: Chem. 765 (2006) 21.
[72] S.A. Llewellyn, M.L.H. Green, Dalton Trans. (2006) 4164.
[73] J. Andrieu, J.M. Camus, C. Balan, P. Proli, Eur. J. Inorg. Chem. (2006) 62.
[74] G.W. Liu, C.Z. Li, L.F. Guo, M. Garland, J. Catal. 237 (2006) 67.
[75] X.L. Luo, D.Y. Tang, M. Li, Int. J. Quant. Chem. 106 (2006) 1844.
[76] M. Basato, A. Biffis, G. Martinati, C. Tubaro, C. Graiff, L.A. Tripicchio, A. Aronica, A.M. Caporusso, J. Organomet. Chem. 691 (2006) 3464.
[77] N. Yoshikai, M. Yamanaka, I. Ojima, K. Morokuma, E. Nakamura, Organometallics 25 (2006) 3867.
[78] L.A. Aronica, P. Raffa, G. Valentini, A.M. Caporusso, P. Salvadori, Eur. J. Org. Chem. (2006) 1845.
[79] L.A. Aronica, P. Raffa, G. Valentini, A.M. Caporusso, P. Salvadori, Tetrahedron Lett. 47 (2006) 527.
[80] T.O. Vieira, M.J. Green, H. Alper, Org. Lett. 8 (2006) 6143.
[81] A.J. Pardey, F. Hung-Low, G.C. Uzcategui, M.C. Ortega, C. Longo, React. Kinet. Catal. Lett. 88 (2006) 203.
[82] E.G. Chepaikin, A.P. Bezruchenko, K.A. Suerbaev, K.M. Shalmagarnbetov, Petrol. Chem. 46 (2006) 117.
[83] V.A. Averyanov, N.M. Nosova, S.A. Batashev, Petrol. Chem. 46 (2006) 99.
[84] J.K. Liu, B.T. Heaton, J.A. Iggo, R. Wyman, J.F. Bickley, A. Steiner, Chem. Eur. J. 12 (2006) 4417.
[85] A.M. Kalsin, N.V. Vologdin, T.A. Peganova, P.V. Petrovskii, K.A. Lyssenko, F.M. Dolgushin, J. Organomet. Chem. 691 (2006) 921.
[86] C. Tortosa-Estorach, N. Ruiz, A.M. Masdeu-Bulto, Chem. Commun. (2006) 2789.
[87] V.A. Averyanov, S.A. Batashev, N.T. Sevostyanova, N.M. Nosova, Kinet. Catal. 47 (2006) 375.
[88] E. Guiu, M. Caporali, B. Munoz, C. Muller, M. Lutz, A.L. Spek, C. Claver, P.W.N.M. van Leeuwen, Organometallics 25 (2006) 3102.
[89] A. Balázs, C. Benedek, S. Tőrös, J. Mol. Catal. A: Chem. 244 (2006) 105.
[90] G. Rangits, L. Kollár, J. Mol. Catal. A: Chem. 246 (2006) 59.
[91] J.J.M. de Pater, B.J. Deelman, C.J. Elsevier, G. van Koten, J. Mol. Catal. A: Chem. 258 (2006) 334.
[92] C. Godard, A. Ruiz, C. Claver, Helv. Chim. Acta 89 (2006) 1610.
[93] A. Ionescu, M. Ruppel, O.F. Wendt, J. Organomet. Chem. 691 (2006) 3806.
[94] A. Ionescu, G. Laurenczy, O.F. Wendt, Dalton Trans. (2006) 3934.
[95] M. Karlsson, A. Ionescu, C. Andersson, J. Mol. Catal. A: Chem. 259 (2006) 231.
[96] A.J. Rucklidge, G.E. Morris, A.M.Z. Slawin, D.J. Cole-Hamilton, Helv. Chim. Acta 89 (2006) 1783.
[97] B.C. Zhu, X.Z. Jiang, Appl. Organomet. Chem. 20 (2006) 277.
[98] S. Doherty, J.G. Knight, M. Betham, Chem. Commun. (2006) 88.
[99] J. Liu, J. Chen, C. Xia, J. Mol. Catal. A: Chem. 250 (2006) 232.
[100] A. Lapidus, O. Eliseev, T. Bondarenko, N. Stepin, J. Mol. Catal. A: Chem. 252 (2006) 245.
[101] P. Giannoccaro, D. Cornacchia, S. Doronzo, E. Mesto, E. Quaranta, M. Aresta, Organometallics 25 (2006) 2872.
[102] G. Lesma, A. Sacchetti, A. Silvani, Synthesis-Stuttgart (2006) 594.
[103] C.M. Kormos, N.E. Leadbeater, Synlett (2006) 1663.
[104] A. Gniewek, J.J. Ziolkowski, A.M. Trzeciak, L. Kempinski, J. Catal. 239 (2006) 272.
[105] W. Zawartka, A.M. Trzeciak, J.J. Ziolkowski, T. Lis, Z. Ciunik, J. Pernak, Adv. Synth. Catal. 348 (2006) 1689.
[106] I. Pryjomska, H. Bartosz-Bechowski, Z. Ciunik, A.M. Trzeciak, J.J. Ziolkowski, Dalton Trans. (2006) 213.
[107] X.D. Zhao, H. Alper, Z.K. Yu, J. Org. Chem. 71 (2006) 3988.
[108] H. Neumann, A. Brennfuhrer, P. Grob, T. Riermeier, J. Almena, M. Beller, Adv. Synth. Catal. 348 (2006) 1255.
[109] Y. Horino, N. Wakasa, T. Fuchikami, T. Yamakawa, J. Mol. Catal. A: Chem. 258 (2006) 152.
[110] P. Berger, A. Bessmernykh, J.C. Caille, S. Mignonac, Synthesis-Stuttgart (2006) 3106.
[111] Q. Lin, H.Y. Fu, M.L. Yuan, H. Chen, X.J. Li, Acta Phys. Chim. Sinica 22 (2006) 1272.
[112] C.X. Cai, N.R. Rivera, J. Balsells, R.R. Sidler, J.C. McWilliams, C.S. Shultz, Y.K. Sun, Org. Lett. 8 (2006) 5161.
[113] C. Liu, R.A. Widenhoefer, Chem. Eur. J. 12 (2006) 2371.
[114] P. Ács, E. Müller, G. Czira, S. Maho, M. Perreira, L. Kollár, Steroids 71 (2006) 875.
[115] F.G. Ye, H. Alper, Adv. Synth. Catal. 348 (2006) 1855.
[116] K.S. Müller, F. Koc, S. Ricken, P. Eilbracht, Org. Biomol. Chem. 4 (2006) 826.
[117] M. Ahmed, R.P.J. Bronger, R. Jackstell, P.C.L. Kamer, P.W.N.M. van Leeuwen, M. Beller, Chem. Eur. J. 12 (2006) 8979.
[118] Y.Y. Wang, J.H. Chen, M.M. Luo, H. Chen, X.J. Li, Catal. Commun. 7 (2006) 979.
[119] Y.Y. Wang, M.M. Luo, Q. Lin, H. Chen, X.J. Li, Green Chem. 8 (2006) 545.
[120] Y. Li, H. Alper, Z.K. Yu, Org. Lett. 8 (2006) 5199.
[121] B. Gabriele, G. Salerno, L. Veltri, R. Mancuso, Z.Y. Li, A. Crispini, A. Bellusci, J. Org. Chem. 71 (2006) 7895.
[122] A. Mansour, M. Portnoy, J. Mol. Catal. A: Chem. 250 (2006) 40.

[123] X.Y. Wu, J. Wanneberg, M. Larhed, Tetrahedron 62 (2006) 4665.
[124] X.Y. Wu, J.K. Ekegren, M. Larhed, Organometallics 25 (2006) 1434.
[125] J.R. Martinelli, D.M.M. Freckmann, S.L. Buchwald, Org. Lett. 8 (2006) 4843.
[126] E. Takács, R. Skoda-Földes, P. Ács, E. Müller, G. Kokotos, L. Kollár, Lett. Org. Chem. 3 (2006) 62.
[127] P. Ács, E. Müller, G. Rangits, T. Loránd, L. Kollár, Tetrahedron 62 (2006) 12051.
[128] B.C. Zhu, X.Z. Jiang, Synlett (2006) 2795.
[129] K.W. Yang, X.Z. Jiang, Bull. Chem. Soc. Jpn. 79 (2006) 806.
[130] K.-D. Wiese, D. Obst, Top. Organomet. Chem. 18 (2006) 1.
[131] A.M. Trzeciak, J.J. Ziolkowski, Przem. Chem. 85 (2006) 96.
[132] A. Riisager, R. Fehrmann, M. Haumann, P. Wasserscheid, Top. Catal. 40 (2006) 91.
[133] S. Bektesevic, A.M. Kleman, A.E. Marteel-Parrish, M.A. Abraham, J. Supercrit. Fluids 38 (2006) 232.
[134] G. Varchi, I. Ojima, Curr. Org. Chem. 10 (2006) 1341.
[135] J.J.M. Pater, B.J. Deelman, C.J. Elsevier, G. van Koten, Adv. Synth. Catal. 348 (2006) 1447.
[136] E. Alacid, D.A. Alonso, L. Botella, C. Najera, M.C. Pacheco, Chem. Rec. 6 (2006) 117.