

Review

Progress in hydroformylation and carbonylation

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Abstract

The last 15 years of hydroformylation and carbonylation chemistry are reviewed, including technical and commercial aspects.

Keywords: Carbonylation; Hydroformylation; Homogeneous catalysis; Organometallic complexes

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1. Introduction

Over the past 15 years since Falbe's 'New Syntheses with Carbon Monoxide' [1], many monographs on the partial aspects of syngas chemistry but no comprehensive presentation of the progress and development trends in hydroformylation and carbonylation have been published [2–8]. Therefore this paper will provide a survey of the focal points of both types of syntheses and their industrial relevant developments since approx. 1980.

In 1980, *hydroformylation*, which celebrated its 50th anniversary [6] in 1988, was a ripe technology with worldwide capacities of 5.2×10^6 tons per year [1] (1965: 0.8×10^6 t [9], 1995: over 6.6×10^6 t, cf. Section 2.4.1.). Surprisingly, the product range of technical hydroformylation (*oxo synthesis*, *Roelen reaction*) has remained nearly unchanged for the past 15 years, although between 1965 and 1980 a remarkable diversification of products, refinement of methods and further development of the Co-based processes took place as did the initial penetration and substitution of these processes by Rh-based catalysts [10]. As compared to less than 10% in 1980, in 1995 nearly 80% of all oxo products will be produced using Rh catalysts (over 90% in the case of propylene hydroformylation, [11], cf. Section 2.4.).

This surprising change in the process basis of a technology, which already took place in 1980, can be compared only with the groundbreaking conversions of the *carbonylation* reaction to acetic acid, either by substituting the metal base of methanol carbonylation from cobalt to rhodium or changing the feedstock from ethylene (via

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acetaldehyde) to methanol. It may be assumed that the hydroformylation and carbonylation processes will undergo other similar fundamental changes as far as reaction engineering is concerned. In addition, the carbonylation business may be affected by considerable extensions of the product range. Some of these developments are already discernible and will determine the R&D work of oxo and carbonylation laboratories in industry as well as at universities (cf. Section 4.).

As far as the hydroformylation and carbonylation processes are concerned, the past 15 years were marked by several (partly in parallel) developments of great economic significance:

1. The substitution of the catalyst's central atom cobalt by rhodium may have been obvious or even overdue since Schiller's and Esso's patent applications [12]. Nevertheless, a hydroformylation catalyst metal as Rh did not become important, economically or technically viable until the success of UCC [13] in 1976 and prior efforts of the former Celanese Corp. [14]. As regards the carbonylation and the manufacture of acetic acid, the move from cobalt to rhodium (Monsanto versus BASF process) took place in the early seventies and the switch from ethylene (via acetaldehyde) to methanol as feedstock is currently under way. Other processes lost their importance or diminished in significance, e.g. the homogeneously and with $\text{Ni}(\text{CO})_4$ catalyzed Reppe-carbonylation of acetylene to acrylic acid versus the *heterogeneously* catalyzed vapour phase *oxidation* of propylene.

While oxo syntheses are determined only by Co and Rh catalysts, the range of the carbonylation products – formerly based on Co, Ni, Pd and Rh catalysts – has now been extended by Se, Cu, Fe, Ru, Ir, Pt, Ag or Mn and others as central atoms of appropriate complex catalysts.

2. While the industrially relevant product range of hydroformylation has remained more or less unchanged over the past 15 years, the research work on carbonylation reactions has continued to diversify. Isocyanates by carbonylation of nitro compounds or amines, anthraquinone from benzene, vinyl acetate from methyl acetate or different carboxylic acids (adipic acid from butadiene, terephthalic acid from toluene, trimellith acid from *m*-xylene) are based on processes which in some cases will be introduced into technical operation [15]. Besides these industrially relevant processes, R&D work on carbonylation chemistry has provided a wide range of techniques for specialties such as ethylene/CO copolymers, succinic acid esters, acrylic acids and profenes, sarcosinates, and others. Other important and technically viable syntheses may be expected.

3. The variations of the central atoms are accompanied by modifications of the ligands. The complex catalysts for hydroformylation and carbonylation reactions profited considerably from advanced knowledge of the correlations between central atoms and ligands on the one hand and their activity and selectivity relationships on the other hand. Today's customary 'tuning' of catalysts would not be possible without the deep insights into ligands of complex catalysts or the experiences acquired in industrial productions such as the Monsanto (to acetic acid), Union Carbide or Ruhrchemie/Rhône-Poulenc (oxo) processes. The development of a generation of more active and more effective ligands is underway in various industry and university laboratories. This is especially true of stereoselective catalysts.

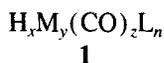
4. As far as technical procedures and modifications are concerned the last 12 years demonstrated the breakthrough of biphasic processes [16], which were prophesied by Manassen back in 1972 [17] and have proved their significance and efficacy in producing higher olefins (Shell's SHOP process [18]), stereoselectively hydrogenated substrates (*L*-Dopa, Monsanto, [19]), phenyl acetic acids (Montedison, [20]) or oxo aldehydes (Ruhrchemie/Rhône-Poulenc, [21]). Thus, the problem of a 'heterogenization' of homogeneous catalysts, important scientifically as well as economically, has been solved in principle. Other methods which involved a variation of the application phase and thus a heterogenization or 'immobilization' by precipitation of the catalytical active species on supports ('anchoring') remained unsuccessful.

Special and more economically inclined developments with hydroformylation or carbonylation reactions can only be mentioned briefly, such as the discussions about toxicities of different oxo plasticizer alcohols (which is controlled by competitive interests), the expansion of the products derived from the methanol carbonylation of acetic acid to acetic anhydride and thus the economically important change in licensing rights from Monsanto to BP etc.

2. Hydroformylation

2.1. Catalysts

Hydroformylation catalysts typically consist of a transition metal atom (M) which enables the formation of metal–carbonyl hydride species. Optionally, these complexes are modified by additional ligands (L). A general composition is represented by the structure



The active hydroformylation species may be formed by precursors of different composition. Even transition metal chlorides have been shown to be active as they are converted under syngas pressure and high temperature to species defined by the above mentioned formula.

The application of two or more metals, homo- or bimetallic, will be discussed in Section 2.1.1.2. Improvements of the catalyst's performance have mainly been achieved by variation of the modifying ligands which will be discussed in Section 2.1.2. Since the last in-depth review in 1980 [22] more than 150 papers and patents on hydroformylation have appeared annually. In 1994 alone, the CAS reviewed 234 publications in this area [23]. The following sections will therefore discuss the recent developments using carefully selected examples.

2.1.1. Variation of the central atom

2.1.1.1. Monometallic catalysts

Modern hydroformylation research focuses almost exclusively on the metals cobalt, rhodium, and platinum although considerable effort also went into ruthenium catalysts [24]. The generally accepted order of hydroformylation activity with regard to the central metal atom clarifies this picture [25]:



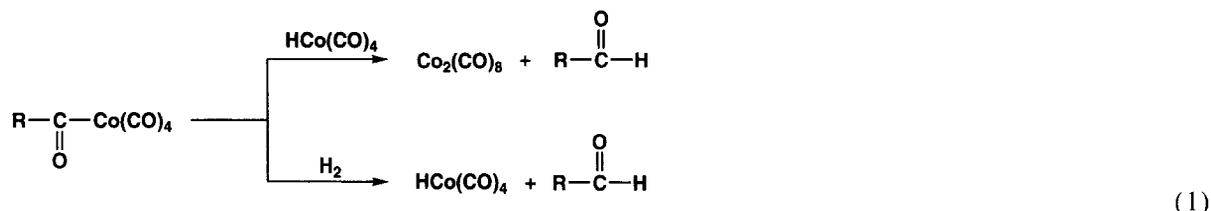
Commercial hydroformylation plants are run exclusively with catalysts based on Rh or Co, namely $\text{HCo}(\text{CO})_4$, $\text{HCo}(\text{CO})_3\text{PBU}_3$ and $\text{HRh}(\text{CO})(\text{PR}_3)_3$ [26] (cf. Section 2.4.).

Up to now, platinum and ruthenium catalysts are mainly of academic interest. Tin(II) chloride modified platinum catalysts have significantly gained importance in the field of asymmetric hydroformylation. Many other carbonyl forming transition metals have been claimed to be active in the oxo reaction, for instance Mo [27,29] (c), Cr [27], Mn [28], Tc [32], Ir [31], Fe [29] or Os [30]. However, activities and lifetimes of these catalysts are inferior to those achieved with Rh, Co, Pt or Ru. A comparison of phosphine modified and unmodified Co, Rh, Ru, Os and Ir carbonyls in the hydroformylation of propene can be found in [22]. A more recent work compares group 8 and group 9 transition metals in the hydroformylation of 1-hexene and confirms the above-stated order of reactivity [33].

Today the main activities of hydroformylation research are in the fields of ligand syntheses and modified catalysts. However, unmodified complexes like $\text{HCo}(\text{CO})_4$ [34], $\text{Co}_2(\text{CO})_8$, $\text{Rh}_4(\text{CO})_{12}$ or $\text{Ru}_3(\text{CO})_{12}$ [24] are still the object of detailed studies. This is partly due to their easy availability, their well-known properties and their rather unproblematic handling. Additionally, they serve as much simpler models than modified catalysts. But the main reason for their persistent topicality is the fact that the mechanism of hydroformylation is far from being well understood. Despite its long history, $\text{HCo}(\text{CO})_4$ for instance has been known and applied in the oxo reaction since the early days of Roelen's discovery in 1938 [6,35] yet some points related to the mechanism have still not been clarified in detail [36]. Since Heck and Breslow formulated their generally accepted hydroformylation cycle [37], several questions arose which were the subject of intense discussions during the eighties.

For instance, the reaction of acyl cobalt complexes with hydrogen equivalents and the successive reductive elimination of the aldehyde were debated [38]. For this very last step of the hydroformylation cycle several pathways

are possible, including radical species [39]. The two most plausible pathways for the hydrogenation of an acyl cobalt carbonyl are shown in Eq. 1.



Mirbach stated the reaction of the acylcobalt complex with $\text{HCo}(\text{CO})_4$ to be the minor pathway, whereas the reaction with H_2 dominates the catalytic cycle in the hydroformylation of 1-octene and cyclohexene. Markó, however, found that the hydridocobalt complex reacts twelve times faster with the acylcobalt complex than with hydrogen. Correctly, he stated [38] (a): “...in the long-lasting discussion about the role of H_2 and $\text{HCo}(\text{CO})_4$ in the hydrogenolysis of acylcobalt carbonyls...both views may be correct. ...obviously their relative importance will depend on the structure of the acyl complex.”

This was proven by later work of the same author [38] (e) and undoubtedly – under industrially applied reaction conditions – the hydrogenolysis of the acylcobalt complex is effected exclusively by hydrogen. The remaining hydrido cobalt species is still in question. Besides $\text{HCo}(\text{CO})_3$ the cobalt cluster $\text{HCo}_3(\text{CO})_9$ is discussed [40]. Some work related to the electronic structure of the catalyst [41] contributed to this discussion, for instance light-induced hydroformylation [42], but significant progress in this area is still lacking.

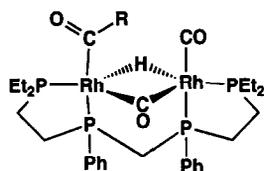
2.1.1.2. ‘Poly’metallic catalysts

Hydroformylation catalysts consisting of more than one metal atom have been thoroughly studied. Especially cluster chemistry contributed a tremendous amount of work in this area before the decline of this sector in homogeneous catalysis became obvious. Numerous publications [43] have shown that clusters used as starting materials are degraded to at least bimetallic species which performs the hydroformylation reaction. The species studied [44] in the past cover homo- and heterometallic, phosphido-bridged and ligand-modified mono and mixed metal clusters. The most recent work by Garland [45] clearly indicates that compounds like $\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$, $\text{Rh}_2(\text{CO})_4\text{Cl}_2$, $\text{CoRh}(\text{CO})_7$ and $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ are degraded to the active transient species $\text{HRh}(\text{CO})_3$ under hydroformylation conditions. The often-mentioned synergistic effect [46] in cluster catalysis is in this case due to the rapid formation of the active catalyst species. The induction period is 2–3 orders of magnitude shorter compared to conventional catalyst precursors. The reaction is exclusively performed by the monomeric Rh species. However, it cannot be excluded that under certain reaction conditions, especially at low temperatures and pressures, the cluster species are more active than their monometallic counterparts [47]. A recent comprehensive review on clusters and hydroformylation can be found in [48].

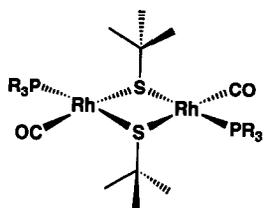
The situation with ligand modified bimetallic catalysts is completely different. The slogan “two metals are better than one” found its way into the literature. Work of Stanley and Kalck in this area suggests that bimetallic catalysts show cooperative effects in the catalytic cycle.

High activities and selectivities in the hydroformylation of 1-hexene ($n/\text{iso} = 96/4$) were reported during the use of the phosphine ligand $\text{CH}_2[\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PEt}_2]_2$ [49]. The proposed active species **2** indicates a cooperative effect of both rhodium centers (structures **2** and **3**). The postulated bimetallic reaction mechanism [50,51] is based on well-established steps, for instance the hydride transfer reaction between two metal centers. Additionally, similar tetra dentate phosphines that prevent a metal–metal interaction by steric reasons show lower or no activity at all. The high rates achieved with **2** at moderate reaction conditions are dramatically decreased if electronically equivalent mono phosphines were used instead of $\text{CH}_2[\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PEt}_2]_2$. The low rates expected for electron-rich ligands were observed in these cases. Altogether, there is strong evidence for a real cooperative effect of the two metal

centers as the results obtained with the bimetallic system are completely different from those achieved with their monometallic counterparts.



2



3

Kalck [52] reported the thiolato bridged complexes $\text{Rh}_2(\mu\text{-SR})_2(\text{CO})_2\text{L}_2$ (**3**) ($\text{R} = \text{'Bu, Ph}$ and $\text{L} = \text{P}(\text{OMe})_3, \text{P}(\text{OPh})_3, \text{PPh}_3$ [= TPP]) to exclusively form aldehydes in oxo-synthesis. No formation of alcohols or condensation products (heavy ends) was observed. Compared to their monometallic derivatives these complexes show high activities in the hydroformylation of 1-hexene. A bimetallic reaction mechanism has been formulated. However, the results are similar to conventional Rh/TPP complexes, so that the true nature of the catalysts might be monometallic. This is supported by work of Southern, which indicates that hydroformylation of 1-hexene shows a half-order dependence on the catalyst concentration [53].

Although both leading research groups in this area argue the true nature of their catalysts, the results are encouraging and seem to replace the cluster parties in this particular field of bi- and polymetallic catalysis. Similar to Kalck's systems, fluorothiolato- [54] and aminothiolato- [55] bridged dinuclear rhodium complexes $[\text{Rh}(\mu\text{-SR})(\text{L})(\text{L}')_2]$ ($\text{L} = \text{L}' = \text{COD}$ or $\text{L} = \text{CO}, \text{L}' = \text{PR}'_3$) have been described as active precursors for the hydroformylation of alkenes under mild conditions (5 atm, 80°C). Recently, the dithiolato-bridged rhodium complexes $\text{Rh}_2(\mu\text{-S}(\text{CH}_2)_n\text{S})(\text{COD})_2$ ($n = 2, 3$ or 4, $\text{COD} = 1.5$ cyclooctadiene) were reported to catalyze the hydroformylation of 1-hexene with and without additional phosphine or phosphite ligands [56]. Bimetallic and bipurpose as well as asymmetric variants of this basic type of catalysts have also been described [57,521].

2.1.2. Variation of the ligand

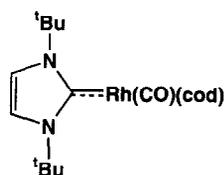
2.1.2.1. Basic principles

As mentioned above, the most active research areas in hydroformylation are ligand synthesis and their coordination chemistry. Considering the developments in the last fifteen years, the lack of a consistent structure–activity relationship is obvious. Very often the catalytic results of sometimes costly synthesized ligands are disappointing. Surprisingly, efforts by the scientific community to overcome this problem has been limited. The intellectually appealing, creative synthesis of sophisticated ligands promises more glory than systematic work on the basics of structure and performance in the oxo reaction. Nevertheless, it is recognized that a general theory is unlikely to be formulated in the near future and if one is, it will be limited to closely related classes of ligands and metal atoms.

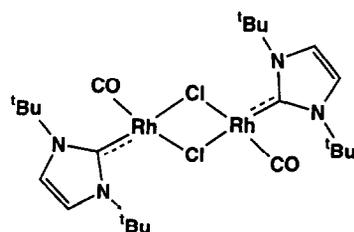
Among the classes of compounds which are able to coordinate to a transition metal and form a complex, phosphines are the most widely used and accepted ligands [58]. Nitrogen containing ligands like amines, amides or isonitriles

showed exclusively lower reaction rates in the oxo reaction due to their stronger coordination to the metal center. Accordingly, water-soluble amine ligands have been used to recover rhodium metal from organic waste streams [59]. The most extensive work on the influence of amine ligands on the hydroformylation of propene with $\text{Rh}(\text{CO})-(\text{PPh}_3)_2\text{Cl}$ can be found in [60]. Schumann and others described mono- and dirhodium complexes with pyrazolato moieties to be active in the hydroformylation of 1-alkenes [61]. Yet selectivities and activities were poor. A comparative study of Ph_3E (E = element of Main Group V) in the hydroformylation of 1-dodecene showed the following order of reactivity: $\text{Ph}_3\text{P} \gg \text{Ph}_3\text{N} > \text{Ph}_3\text{As}, \text{Ph}_3\text{Sb} > \text{Ph}_3\text{Bi}$ proving again the superiority of phosphine ligands [62].

A major breakthrough in the replacement of phosphines was recently achieved by Herrmann et al. [63]. Carbenes obtained from imidazolium salts are surprisingly stable and were isolated in their free form [64]. More than twenty metal complexes have been synthesized, among them the rhodium complexes **4** and **5**. These complexes catalyze the hydroformylation of 1-hexene: It remains to be seen what this new class of ligands will contribute to the hydroformylation reaction in particular and to catalysis in general.



4



5

Due to their extensive use in catalysis, phosphines and their coordination chemistry have been studied in the most detail [58]. Since Tolman's basic work on the cone angles and electronic parameters of phosphines [65] only a few papers appeared dealing with the structure and influence of phosphines on the catalytic results [66]. Bonding and energetics of phosphorus(III) ligands in transition metal complexes have been reviewed [67]. Casey developed the 'natural bite angle' as an additional characteristic of diphosphines based on molecular mechanics calculations [68]. Selectivities for linear versus branched products can now be estimated from the ligand's structure in some cases. The concept of the natural bite angle is generally accepted and used by several other authors [69].

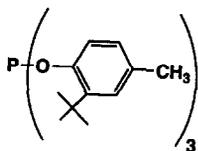
Researchers now have an almost rational understanding of the regioselectivities to be expected, since classifications of ligands in terms of their steric demands are available. Nevertheless, the overall activity of phosphine-modified catalysts remains completely unpredictable. Creative design of basic structures and their subsequent stepwise modifications is still the old-fashioned but successful way to the further development of hydroformylation catalysts. Only a few publications have appeared on the electronic properties of phosphines and their influence on catalytic results [70]. In detailed studies Hughes and Unruh investigated the dependence of the hydroformylation results on the basicity of diphosphine ligands [71]. From a Hammett sigma-rho plot they drew the conclusion that less basic ligands afford higher activities and n/iso ratios.

In this particular area computer assisted design is far from providing any significant insight into the direction ligand synthesis is heading. The rational design of ligands by mathematical methods was described only recently

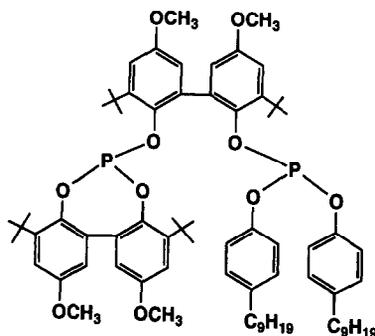
[72]. Phosphines were claimed as ligands based on their electronic and steric properties for the synthesis of hydroxyaldehydes, 2-methyl-1,6-hexane dicarboxylic acid and other compounds [73].

2.1.2.2. Phosphites

In the past few years major progress has been made by using phosphites of the general formula $(RO)_3P$ as ligands in rhodium-catalyzed oxo synthesis. Bulky mono and biphosphites like **6** and **7** have enabled the hydroformylation of long-chained olefins with considerably high activities [74,75].



6



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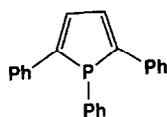
Less reactive olefins like 1-octene, 2,3- and 2,5-dihydrofuran but also 1-butene and 2-butene are hydroformylated at much higher rates compared to those achieved with phosphine-modified catalysts. Due to their steric bulkiness, even in the hydroformylation of 2-butene *n*/*iso* ratios of 96/4 were observed. A detailed kinetic study of a rhodium/**6** catalyst in the hydroformylation of 1-octene, cyclohexene and styrene was published recently [76]. Under moderate reaction conditions high rates were obtained for 1-octene. The rate determining step is in the reaction of H_2 with the acylrhodium complex. Rates with cyclohexene and styrene were much lower. Solution structures of hydrido Rh diphosphite complexes were investigated in detail by NMR spectroscopy [77]. BASF reported the hydroformylation of methyl-3-pentene carboxylate with $Rh(CO)_2(acac)$ and **7** as a ligand. Methyl-5-formyl valerate was formed with 72% selectivity [78].

With respect to the increasing importance of low-volatile plasticizers – the first step in their synthesis being hydroformylation of a long-chained olefin – rhodium phosphite catalysts possess useful properties and will become significant. Their impact on asymmetric hydroformylation will be discussed in Section 2.2.2.

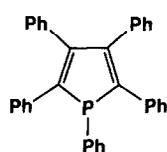
2.1.2.3. Phosphines

The contributions of phosphines to progress in hydroformylation have been rather limited. However, some results are worth discussing. Neibecker, Reau and others introduced phospholes (**8**, **9**) and phosphanorbornadiene (**10**) to oxo synthesis [79–81]. In the case of phospholes, activity and selectivity are independent of the phosphine/Rh

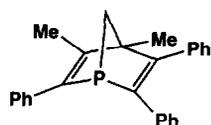
ratio. The phosphanorbornadienes are sterically demanding ligands comparable to triphenylphosphine (TPP) (Tolman's cone angle θ : 147° vs. 145° for TPP). Therefore the regioselectivities in the hydroformylation of 1-hexene and styrene are similar to those obtained with TPP, but activities are five times higher [79]. Recently the phosphanorbornadiene **10** was sulfonated and successfully applied in the two-phase hydroformylation of propene and 1-hexene [82].



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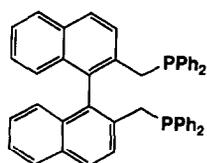


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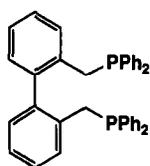


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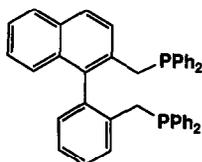
In recent years Eastman Kodak has become a major player in the development of new phosphine ligands for oxo synthesis. Based on the principle of NAPHOS (**11**) [83] the derivatives BISBI (**12**) and PHENAP (**13**) were developed [84]. These ligands show considerable activity and extremely high regioselectivity in the hydroformylation of 1-hexene (Table 1) at moderate syngas pressures. Normal to branched ratios of 96/4 were observed at very low phosphine/Rh ratios. These results were the starting point in the development of the water-soluble ligands BISBIS and BINAS based on these diphosphines for the Ruhrchemie/Rhône-Poulenc process.



11



12



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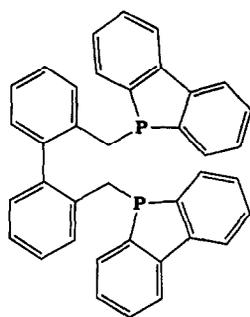
Recently even higher regioselectivities were claimed by Eastman Kodak. By combining the basic biaryl structure of BISBI with dibenzophosphole moieties, ligands **14** (2,2'-bis(dibenzophospholymethyl)-1,1'-biphenyl) and **15** (2,2'-bis(dibenzophospholymethyl)-5,5'-di-*tert*-butyl-1,1'-biphenyl) were made accessible independently by Hoechst and Eastman Kodak [85]. In the rhodium catalyzed hydroformylation of propene with **15**, n/iso ratios of 99.6/0.4 (!) were observed. This means exclusive formation of the n-butyraldehyde. The rates were considerably high (1.2 kg aldehyde/g Rh · h⁻¹). With ligand **14** 1-octene was transformed to nonanal at a n/iso ratio of 98/2. However, product distributions were not reported [85](a) and preliminary results show fast deactivation of the applied rhodium catalysts [85](c).

Table 1
Comparison of the hydroformylation of 1-hexene^a with TPP, BISBI and NAPHOS

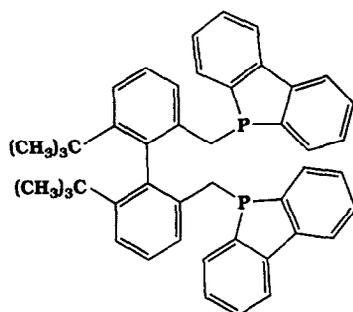
Phosphine	P/Rh ratio	Activity ^b	Selectivity
TPP	124:1	4.27	70:30
BISBI	4.8:1	2.63	96:4
NAPHOS	5:1	2.66	95.5

^a T = 125°C, 260 psi CO/H₂.

^b Activity = [kg (heptanal)/g (Rh) · h].



14



15

Polydentate phosphines were reviewed extensively in 1992 and 1994 [86] with respect to their synthesis, coordination chemistry and application in catalysis. Yet their use in oxo synthesis is limited as they show much lower activities than their monodentate derivatives. Additionally, the regioselectivities are not as high as expected for these bulky ligands. Horváth showed that under syngas pressure and room temperature the tripod ligand $\text{CH}_3\text{C}[\text{CH}_2\text{PPh}_2]_3$, undergoes an ‘arm-off’ dissociation to generate a free coordination site for an incoming CO molecule [87]. This clearly demonstrates the kinetic lability versus the thermodynamic stability of metal–phosphorus bonds in chelating polyphosphine complexes. Aside from similar basic investigations, polydentate phosphines with the exception of Stanley’s system (see above) and have not contributed much to progress in the hydroformylation area.

Triphenylphosphine oxide, long considered as being inactive in oxo synthesis, has been described by several authors to be an efficient ligand despite its weak coordination to metal centers. In 1987 Mitsubishi Kasei launched a 30,000 t/year plant for the production of isononyl alcohol by hydroformylation of octenes [88]. The basic catalyst is a rhodium–triphenylphosphine oxide (TPPO) complex which is stabilized after the oxo reaction by addition of triphenylphosphine (TPP) to permit product distillation without decomposition (cf. Section 2.4.3.).

Amer reported the beneficial effect of phosphine oxides in P–N bidentate ligands on the Rh-catalyzed hydroformylation of styrene [89] (a), which has been confirmed by Bottheghi [89] (b). The ligand $\text{Ph}_2\text{PCH}_2\text{NMe}_2$ showed 59% conversion at 94/6 i/n ratio, whereas with the corresponding oxide $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{NMe}_2$ conversions of 100% (80% after 1 h) and selectivities of 91/9 were observed under identical conditions. Those effects are not yet well understood, but it remains to be seen whether mixed bidentate ligands (P–N, P–O or P–S), with or without an oxidized phosphorus atom, generate a basic understanding of these results in the future. So far these ligands have not been intensively dealt with in the oxo literature [90].

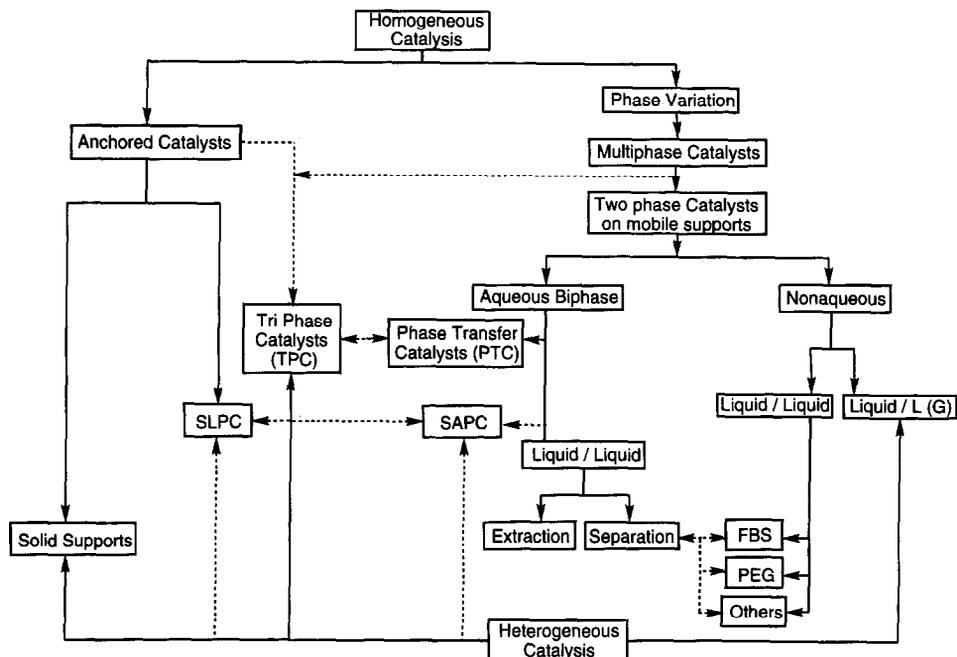
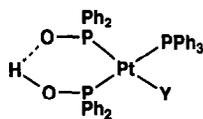


Fig. 1. Different approaches to the variation of the application phase of oxo catalysts (FBS = fluorous biphasic system; PEG = poly ethylene glycol).

Some interesting results with diphenyl phosphinous acid $\text{Ph}_2\text{P}(\text{O})\text{H}$ as a ligand in the Pt and Rh catalyzed hydroformylation were reported by van Leeuwen and others [91,92]. No SnCl_2 modifier or promoter has to be added in order to form an active Pt based oxocatalyst. With catalysts of type **16**, heptenes were hydroformylated to give octanals with 90% linearity. However, hydrogenation was considerable and C_8 alcohols and heptane were also formed. By using ethylene, compounds **16a** ($\text{Y} = \text{C}_2\text{H}_5$) and **16b** ($\text{Y} = \text{C}(\text{O})\text{C}_2\text{H}_5$) were isolated and characterized. Without addition of phosphine, ethylene produced mainly 3-pentanone under hydroformylation conditions.



16 a, b

2.1.2.4. Water-soluble phosphines

Synthesis of water-soluble phosphines today is one of the most active areas in hydroformylation research. Oxo synthesis in a two-phase system with water-soluble catalysts, the Ruhrchemie/Rhône-Poulenc process, will be discussed in detail in Sections 2.1.3.2. and 2.4.2.2. Since the last exhaustive reviews in 1992/93 on water-soluble complexes [93], some progress has been made in this area, which will be discussed here.

Herrmann et al. developed a new and efficient technique to sulfonate phosphines without oxidation of the phosphorus atom [94]. By addition of boric acid to concentrated sulfuric acid and oleum, a super acidic medium is generated which forms the sulfonating agent H_3SO_4^+ . The phosphorus atom is protected against oxidation by protonation, and sulfonation temperatures higher than 60°C are applicable. Therefore, the reaction is more selective towards higher sulfonation degrees. For instance the eight-fold sulfonated NAPHOS, BINAS-8 (**17**), has been obtained in 91% yield. Shorter reaction times at higher temperatures made the two-fold sulfonated triphenylphos-

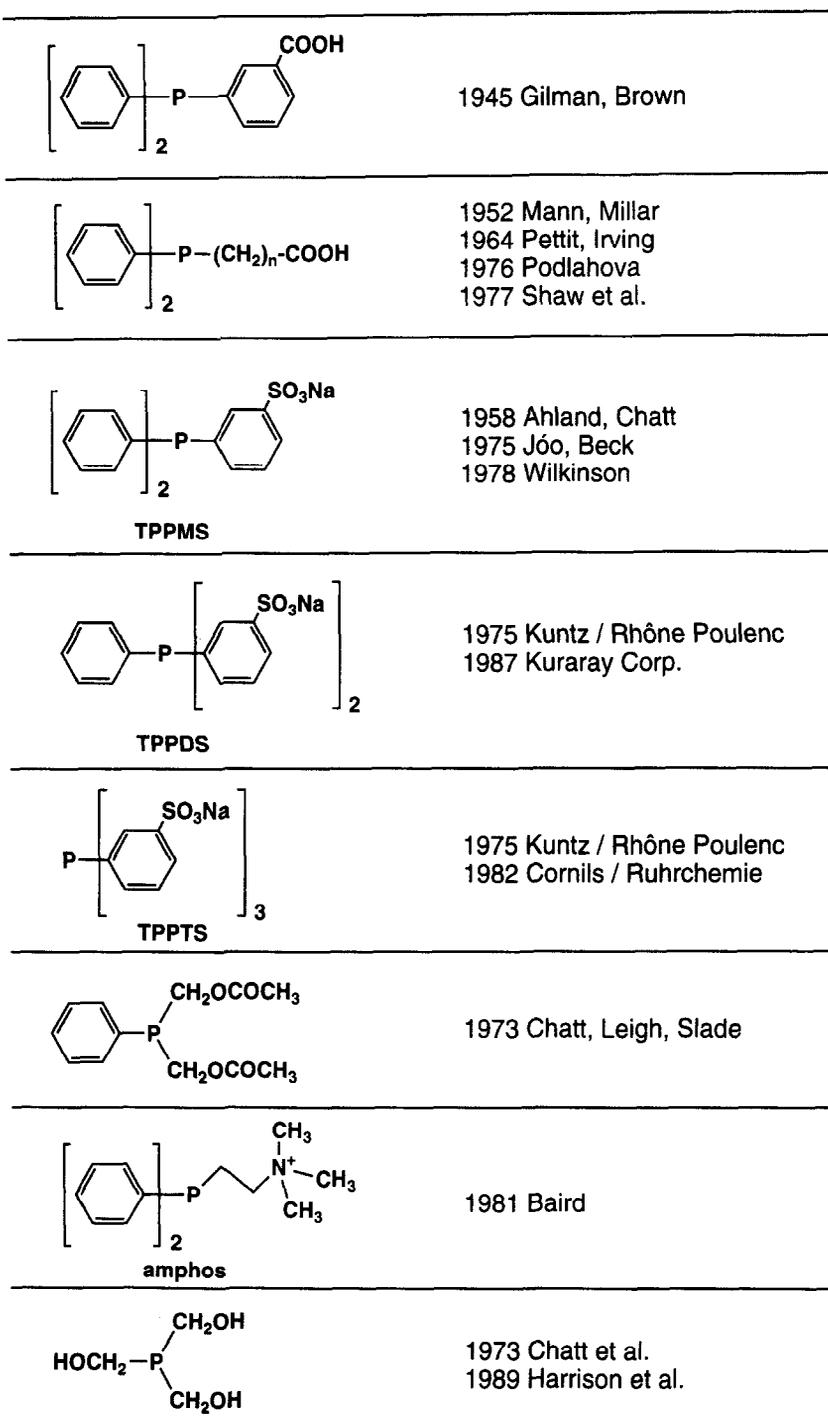
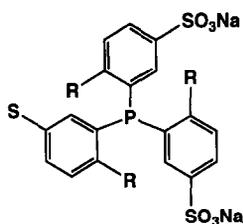
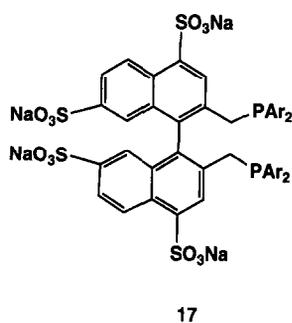


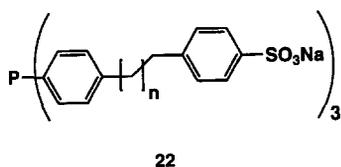
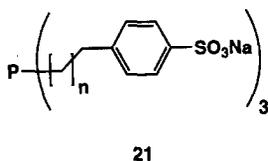
Fig. 2. Water-soluble ligands for oxo homogeneous catalysts [117–123].

phine, TPPDS (18), accessible. TPPMS and TPPTS were not formed. Also trisulfonated tri-*o*-tolylphosphine (19) or tris-*o*-methoxyphosphine (20) were synthesized accordingly (structures 17–20).



- 18: S = H, R = H
 19: S = SO₃Na, R = CH₃
 20: S = SO₃Na, R = OCH₃

Hanson synthesized surface-active phosphines **21** and **22** and metal complexes thereof [95] to study the influence of self-association of water-soluble ligands on catalysis. **22** forms aggregates in aqueous salt solutions, whereas TPPTS shows no evidence of aggregation to a uniform size. The structures change their sizes depending on the salt concentration. The species which aggregate form more active Rh catalysts in the hydroformylation of 1-octene than TPPTS. Furthermore, addition of salt to catalysts derived from surface-active phosphines improves the reaction rate while the rate drops significantly when salt is added to the TPPTS catalyst [95] (d). Differences in catalytic activities ('salt-effect') discovered by Basset [96] might be a result of these self-association effects of water-soluble catalysts.

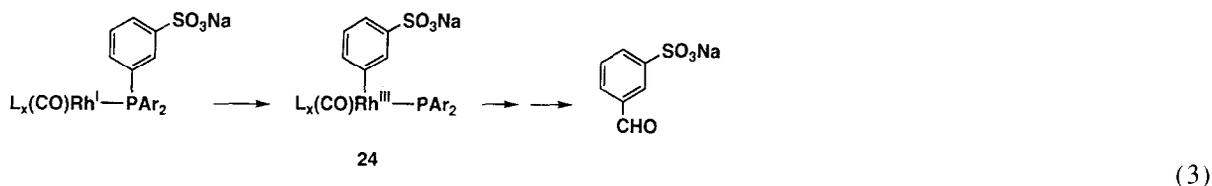


2.1.2.5. Deactivation mechanism of rhodium–phosphine catalysts

One important field in industrial hydroformylation research is the deactivation of rhodium–phosphine catalysts used commercially. As is generally accepted now, the loss of activity with time is due to degradation reactions of the ligand. This issue will therefore be discussed briefly here.

The deactivation mechanism is initiated by the oxidative insertion of the Rh metal into the P–C bond of the TPP ligand (Eqs. 2 and 3). It has been clearly shown by different authors [97] that the equally discussed process of ortho-metallation plays no role. Most of the phosphorus containing by-products formed under continuous operation modes are explainable by subsequent reactions of the aryl–rhodium species **23** (UCC process). For instance $C_3H_7PPh_2$ and phosphinous acid have been identified.

Confirmation of this mechanism was provided by the Ruhrchemie/Rhône-Poulenc process, where the position of the sulfonato group is an outstanding test for oxidative addition versus ortho-metallation [93] (a). The formation of the Na salt of *meta*-formyl benzene sulfonic acid, *m*-OHCC₆H₄SO₃Na, indicates that the Rh atom is temporarily attached to the carbon atom, where the phosphorus atom was bonded before. CO insertion and reductive elimination generates the formylated benzene sulfonic acid from **24**.



This is an interesting example in which the answer to an old question came from industrial researchers. Driven by the need to explain the small deactivation observed in their well-known processes, it was clearly shown by them that ortho-metallation is negligible and P–C bond cleavage by oxidative addition of the metal center and aryl migration is responsible for the ligand degradation.

2.1.3. Variation of the application phase

2.1.3.1. General

Besides influencing the electronic and steric properties of the organometal complex catalysts by means of suited central atoms or ligands the *variation of the application phase* has been the subject of intense work in oxo research since the very beginning. Having originally not recognized the nature of catalysis, the early oxo researchers started the hydroformylation reaction in a heterogeneous mode using fixed beds of Fischer–Tropsch catalysts [35] – the other way to vary the application phase. Accordingly, appropriate techniques (‘diaden’ or ‘two-tower’ process [98]) have been used for longer periods since they enable an apparently elegant separation of catalyst and product.

Together with the necessity of a low-cost separation of catalyst and product, this shortcoming of homogeneous catalysis has provided the impetus to try the homogeneous mode with ‘heterogenized’, ‘immobilized’, or ‘anchored’ catalysts. Fig. 1 demonstrates the different approaches schematically.

Fundamental distinction must be made between ‘anchored’ catalysts (left part of Fig. 1) and the intrinsic phase variation. The anchored catalysts on fixed supports are dealt with in Section 2.1.3.3.2. The more modern and obviously more successful method of phase variation are the ‘multiphase catalysts’ (a modification of which – ‘triphase catalysis’ (TPC, [99,100]) – is a genetic link between heterogeneous and phase-transfer catalysis) as well as ‘two-phase catalysts’, i.e. homogeneous catalysts on ‘mobile’ supports. On the other hand these catalysts are divided into ‘aqueous biphasic systems’ (cf. Section 2.1.3.2.) and ‘non-aqueous biphasic systems’ (2.1.3.3.1). The liquid/liquid biphasic variants, which have already found industrial application as *aqueous biphasic systems* are important. Intense research work is being conducted on liquid/liquid modifications of *non-aqueous systems*, includ-

ing membrane separations [101–103]. Solid/liquid and solid/gaseous variations of non-aqueous catalysts are like ‘solid supported catalysts’ connections between homogeneous and heterogeneous catalysis. Examples of these variations include oxychlorination of methane, vinyl chlorination of ethane, manufacture of monosilane, hydroformylation of ethylene – all in molten salt media [104,105] – catalyst separation as metal [106] or ‘precipitation’ of the catalyst metal from homogeneous polymerizations by grafting of the polymer on the catalyst site or the ‘fouling’ of the apparatus [107].

The transitions of ‘supported liquid phase catalysts’ (SPLC) and ‘supported aqueous phase catalysts’ (SAPC) are dealt with in Section 2.1.3.3.2. Special forms – and in certain aspects a link to phase variation methods – are gaseous phase hydroformylations (e.g. [108]) or shape-selective catalysts for a differential conversion of various alkenes [109]. J6o described a specially tailored version of precursors of SAP catalysts [110].

2.1.3.2. Aqueous catalysts

One of the most important development of the last 15 years in hydroformylation chemistry was the introduction of biphasic homogeneous catalysis. This technique uses a homogeneous catalyst, dissolved in water, as a ‘mobile’ phase (‘mobile support’). By simple phase separation (decantation) the catalyst and reactants/reaction products are separated *just after reaction and approximately at the same temperature*. In relation to the reaction products the catalyst is thus ‘immobilized’ as well as ‘heterogenized’. The many advantages of homogeneous catalysis are thus supported by the argument that catalyst and reaction products may be separated immediately after reaction [15]. This advantageous variation of the application phase normally requires a preceding influence on the organometallic complex by ligand variation.

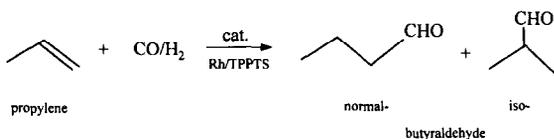
A series of reviews describe biphasic processes in general [16,17,93,111–115]. Following the recommendations of Manassen [17] the history of biphasic hydroformylations began with preparatory work on various water-soluble ligands (c.f. Fig. 2)

The solubility in water is usually achieved by introduction of highly polar substituents such as $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{OH}$, or $-\text{NH}_2$ (or their salts) into the phosphine molecules [17,93,119,125,138]. By varying the kind and the number of suited substituents and by choosing the nature of the aqueous phase nearly any desired ratio of hydrophilic and hydrophobic properties may be adjusted, thus achieving a ‘tailor-made’ set of attributes for complex forming ligands.

After preparatory work on different aspects [124], Kuntz [125] expressed the basic idea of a new generation of water-soluble oxo catalysts with triphenylphosphine trisulfonate (TPPTS, as Na salt, as compared to TPPMS and TPPDS, mono- and disulfonate) as ligands for an Rh-based hydroformylation process. So far TPPTS is the most ideal ligand modifier for the oxo-active $\text{HRh}(\text{CO})_4$. Without any expensive preformation steps, three of the four CO ligands can be substituted by the readily soluble (1200 g/l [126]), non-toxic (LD_{50} , oral: > 5000 mg/kg) TPPTS, which yields the hydrophilic oxo catalyst $\text{HRh}(\text{CO})[\text{P}(m\text{-sulfophenyl-Na})_3]_3$ (cf. Fig. 3)

Together with TPPTS, TPPMS and TPPDS maintain their significance in other applications. With their different grades of sulfonation they allow a fine-tuning of the hydrophilic/hydrophobic ratio of the catalyst during biphasic operation when necessary (e.g. [127,128,522]).

Ruhrchemie AG adapted the idea and applied it to an industrially viable and highly sophisticated process. Thus TPPTS is the basis of the Ruhrchemie/Rhône-Poulenc (RCH/RP) oxo process for the hydroformylation of propylene, which was developed by Ruhrchemie in only two years. The first plant started operation in 1984 (Eq. 4, [129–132]). Approximately 3 million tons of n-butanal have been produced within more than 10 years of experience and prove the importance of the aqueous phase oxo concept. The process was recently licensed [133].



(4)

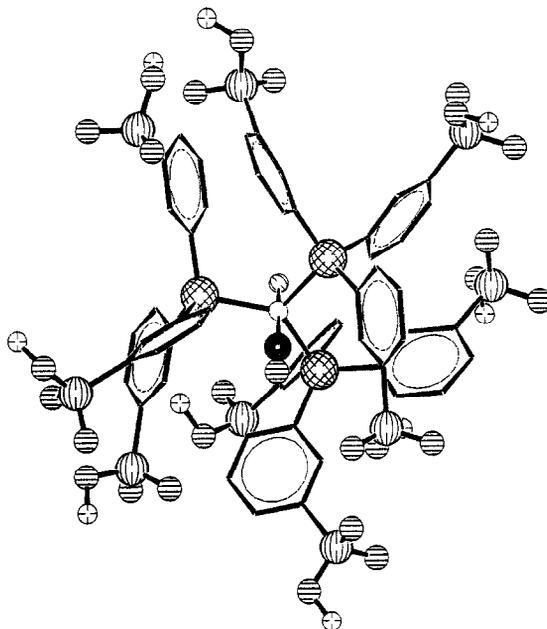


Fig. 3. The oxo-active catalyst $\text{HRh}(\text{CO})[\text{P}(m\text{-sulfophenyl-Na})_3]_3$.

The flow diagram of the RCH/RP process as the most typical example for a biphasic process with organometal, ligand-modified catalyst is shown in Section 2.4.2.2. As a consequence of the solubility of the Rh complex in water and its insolubility in the oxo products the oxo unit is essentially reduced to a continuous batch reactor, followed by a phase separator (decanter) and a strip column (description in [21]). The oxo reaction is smooth and highly efficient as far as activity and selectivity are concerned: the *n*/*iso* ratio is up to 97/3. The catalyst is indeed ‘immobilized’ and Rh losses are low and in the ppb range. The Rh content of the crude aldehyde, which corresponds to losses of less than 10^{-6} g/kg *n*-butanal [21] is also low. This means that the disadvantages of all earlier attempts to ‘anchor’ the homogeneous oxo catalyst on fixed supports (leaching, inactive catalyst species) have been overcome by the biphasic operation with ‘mobile’ supports.

The development of ligands for oxo processes has not come to an end (cf. Section 2.1.2.4.). The work of Herrmann [82](b) may be quoted as one example among others: he introduced different water-soluble ligands such as 17–20. Using these ligands a further improvement in activity and selectivity can be obtained [116,134]. A lot of other contributions to ligand research in oxo chemistry are known, e.g. [15,72,59,93,126,135–145] in respect to other central atoms or other starting olefins including bio-organometallic applications (e.g. [95](a)[146–148,158]). The substitution of Na in TPPTS derived or other processes by Li, K or other cations is claimed to be advantageous (e.g. [149,150]). According to some observations the kinetics of hydroformylations in the aqueous phase may be different to those in non-aqueous media as suspected by Divekar et al. [151].

A relatively poor effect (except for biphasic hydrogenations) has been observed using solely solvents or co-solvents such as EtOH or BuOH as solubilizers for the hydroformylation of *higher olefins* [159–161] (not to mention side-reactions such as e.g. acetal formation during hydroformylation). For example, TPPTS as a standard water-soluble ligand proves especially efficient only in combination with amphiphilic and micelle-forming surfactants together with co-solvents [162]. Years after the pertinent patents had been applied [163] Hanson scientifically reviewed other means such as salt effects, ionic strengths etc. being important for biphasic hydroformylation reactions [95,96,164–166]. Ultrasound treatment is a well suited measure for persistent reactants [167]. According to a proposal of Chaudhari and Delmas et al. even TPP, dissolved in the *organic phase*, acts as a co-solvent and as a co-ligand (‘promotor ligand’) and as reaction rate-increasing additive. The role of mixed complexes like

$\text{HRh}(\text{CO})(\text{TPPTS})_{3-n}(\text{TPP})_n$ is uncertain [168]. The influence of the substrates themselves on the rates of biphasic reactions was discussed by Mortreux et al. [169].

Special aspects, mainly the behavior, control, and organization of the phases of aqueous biphasic processes, are dealt with in separate papers [152–155,522].

In future biphasic processes will play their role in carbonylation chemistry as well (cf. Section 3.1.3.3. [100,156,157]).

2.1.3.3. Other biphasic catalysts

2.1.3.3.1. Non-aqueous systems

Systematically and as shown in Fig. 1 *non-aqueous liquid/liquid systems* of homogeneous catalysis may be used in addition to *aqueous biphasic processes* and demonstrate the same advantages in principle. These benefits are to be distinguished from the discussion whether the ‘catalyst support’ water is environmentally sound, activates the reactants and/or the homogeneous catalysts, or hydrolyzes the metal–ligand bond [136,170–174]. In a classical application Shell’s SHOP process [18,152] (a) [175] uses the immiscibility of two *organic* phases for the separation of catalyst and product: the organometallic complex catalyst, dissolved in butanediol-1,4, is decanted from the reaction product, i.e. higher olefins after ethylene oligomerization. For hydroformylations the use of butanediol has been described e.g. by Kuraray (cf. Section 2.2.1) and Chaudhari/Deshpande et al. [174]. As far as *anchored* catalysts are concerned cf. Section. 2.1.3.3.2.

Horváth’s proposal of a ‘fluorous biphasic (multi-phase) system’ is quite new and based on the miscibility gap of partially or fully fluorinated compounds with non-fluorinated chemicals [136,176,177]. Because of reduced solubilities between both liquid phases (which are dependant on temperature) the reaction (e.g. hydroformylation) takes place at appropriate temperatures in *one* phase. Upon completion of the reaction, the reaction mixture is cooled to room temperature and separates into *two* phases. Thus the application is similar to the Ruhrchemie/Rhône-Poulenc process: after completed hydroformylation the work-up of the reaction mixture consists only of a simple decantation. This easy operation and the unlimited solubility of the starting olefin in the FBS at higher temperatures were highly acknowledged by the R&D community [16,112]. Because of the special nature of FBS – mostly mixtures of perfluorinated hydrocarbons, ethers and tertiary amines – the catalytically active organometallic complexes ought to be specially ‘catalyst tailored’. The Rh complex with ‘ponytailed ligands’ such as $\text{P}[\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3]_3$ [178,179] is an example of these special hydroformylation catalysts.

Obviously, the basic idea of the FBS was described earlier [180], therefore the Exxon patent has to prove its worth. Also the FBS technique has to confirm its suitability during harsh industrial operation. This includes questions of activities, selectivities, life-time and costs of the catalyst system. The consequences of an extraction of the perfluorinated phase by the oxo reaction products (and the resulting problems during subsequent hydrogenation of the oxo aldehydes to plasticizer alcohols) and environmental problems with the handling of FBS (ozone depletion potential [ODP] and greenhouse warming potential [GHWP] of the fluorine-containing compounds) have to be investigated.

The miscibility gap is important for the use of polyalkylene glycols as only partially miscible liquids and as the second phase in non-aqueous systems. Similar to FBS a reaction system with the ‘immobilized’ catalyst, dissolved in alkylene or polyalkylene glycols, can be realized [181]. Taking hydroformylation as an example, the immobilized catalyst remains in the reactor using the partial immiscibility of the oxo reaction products and the glycols. This system requires special ligands for the oxo catalysts as well, e.g. $\text{HRh}(\text{CO})[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{SiR}_3]$ or $\text{HRh}(\text{CO})[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}^+\text{Ph}_2(\text{CH}_2\text{P})\text{BPh}_4^-]_3$. In addition, catalysts with diol or polydiol ligands have been described [137,182]. Those ligands make possible a combination of the aqueous biphasic with non-aqueous reactions [183].

Another approach is the use of the ‘cloud points’ of P-bonded polyalkylene glycol ethers which serve as ligands for oxo active complex catalysts (structure **25**, [137,184]). Above their cloud point these compounds lose their hydrate shell, thus becoming water-insoluble and ensuring a hydroformylation in the organic phase of water-

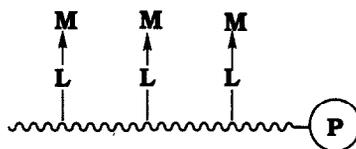
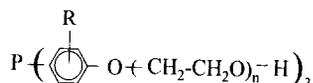


Fig. 4. Basic principles of anchored catalysts. Polymer-supported catalyst, L = ligand, M = metal, P = polymer support.

immiscible olefins. On reducing the temperature the hydrate shell is reversibly restored and the complex returns to the water phase [184].



Finally Bergbreiter et al. described similar ‘smart ligands’ [185], cationic Rh complexes with polyalkylene oxide substituted bis-(2-diphenylphosphinoethyl) amides, dissolved in polyalkylene oxides. These complexes have inverse temperature-dependent solubilities with water. The reaction rate for hydrogenations are high at lower temperatures, while on heating the reaction stops and the phases separate. An SAPC analogue with water-soluble Ru complexes dissolved in ethylene glycol and supported on controlled pore glass has been reported for enantiomeric hydrogenations by Wan and Davies [186] (cf. Section 2.2.2.). For a conversion of this biphasic technique to hydroformylation or carbonylation reactions cf. Section 2.2.1.

Application of this combination of SLPC and SAPC techniques on an industrial scale is rather questionable and hymns of praise [187] seem to be premature. A review of other non-aqueous systems and technical solutions of the catalyst cycle of biphasic liquid/liquid systems is given in [152,188].

2.1.3.3.2. Anchored catalysts

Anchored catalysts [189] are well-defined metal complexes which are bound to a solid support. Examples are polymer-bound metal complexes and SLPC (supported liquid phase catalysts), where the catalyst is immobilized in a thin adsorbed film of a solvent on a solid support. If the solvent is water and a water-soluble complex is used, these catalysts are referred to as SAPC (supported aqueous phase catalysts). This discussion does not include heterogeneous catalysts with precipitated metal salts or metal conglomerates as active species, for instance made by impregnation of a carrier with a metal complex solution and successive reduction to form metal particles. The basic principles can be seen in Fig. 4 and Fig. 5. The interaction between the support and the metal complex is either coordination by an immobilized coordinating ligand or the immobilization in a liquid phase which is adsorbed on the carrier.

2.1.3.3.2.1. *Polymer-supported catalysts.* The immobilization of an expensive catalyst applied in a homogeneous reaction is desirable. Separation of products from the catalyst is easy to achieve and thus decomposition induced by distillation or other methods of recovery is avoided. Organic polymers have been used to graft metal complexes on an insoluble support. It was shown in the seventies [190] that such catalytic systems perform the hydroformylation reaction with improved selectivity for the linear product. However, these catalysts suffer from metal losses through leaching, especially when coordinating solvents are used in the catalytic reaction. Additionally, most polymers used as supports are sensitive to high reaction temperatures. The synthesis, properties and the use of polymer supported metal complexes have been described in two reviews by Pittman [191] and Gates [192].

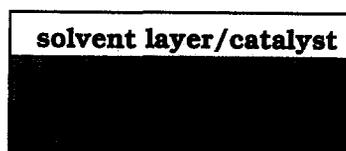
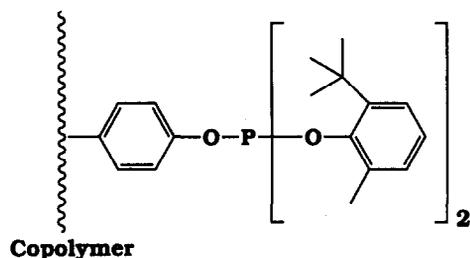


Fig. 5. Basic principles of anchored catalysts. SLPC.

From the basic understanding of the hydroformylation mechanism, it is obvious that the loss of a phosphine ligand is necessary to make a coordination site accessible to reactants for performing the reaction. During the catalytic cycle the metal complex undergoes several changes in structure and coordination number. By fixing the metal center to a support, the possible variations are restricted compared to the 'free' catalyst. Additionally, the metal is more susceptible towards leaching as the fixation is weakened by change of the geometrical structure and number of coordinated ligands. Kalck recently found, that the complex $\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPP})_2$ does not lose a phosphine ligand during the catalytic cycle [52,193]. Consistently this complex was immobilized on a styrene/divinylbenzene polymer functionalized with diphenylphosphino groups to form $\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{Res-PPh}_2)_2$ (Res = resin). The hydroformylation of oct-1-ene showed 90% conversion yielding 84% aldehydes, 4% internal octenes and no hydrogenation. The catalyst was recycled once and performed the reaction with slightly lower rates (1.67 vs. 1.73 min^{-1}) and lower selectivity (89 vs. 91%). A balance of rhodium metal was not reported.

The immobilization of Rh complexes on a styrene–divinylbenzene copolymer which contains $-\text{CH}_2\text{P}(\text{C}_6\text{H}_4\text{SO}_3\text{H})_2-$ groups was described by Ro [194]. In the hydroformylation of propene the activation barrier for these catalysts was 12.1 kcal/mol. With increasing number of sulfonato groups in the polymer the observed activity also increased.

Van Leeuwen was able to attach phosphites to a copolymer chain of styrene/*p*-hydroxystyrene (structure **26**). After fixing rhodium onto the polymer, this anchored Rh–phosphinite catalyst was tested in the hydroformylation of olefins. The activities were comparable to the low molecular weight mononuclear species. However, an equilibrium between the active complex and an inactive species which is not bound to a phosphinite ligand, prohibits the use of the polymer in a continuous flow reactor [195].



Basically, heterogenization of hydroformylation catalysts by bonding to polymer supports is still in its infancy [196]. It is hard to believe from the actual results that they will become a real competitor to homogeneous catalysts. Additionally, the immobilization of metal complexes has been solved by using water-soluble derivatives as liquid supports (cf. Section 2.1.3.2.). However, the recently developed metal–carbene complexes by Herrmann [63] could open a new area of intense research.

2.1.3.3.2.2. *Supported liquid phase catalysts (SLPC)*. Supported liquid phase catalysts (SLPC) for the hydroformylation reaction were extensively studied in the early eighties by Scholten [197] and Hjortkjaer [198]. As shown in Fig. 4 and Fig. 5, the rhodium catalyst, mainly $\text{HRh}(\text{CO})(\text{TPP})_3$, is dissolved in a thin film of a high boiling, low volatile solvent which is adsorbed to a solid support. Examples of such solvents are biphenyl, glycerol tributyrate (GTB), tetraethylene glycol (TEG), polyethylene glycol (PEG), triphenyl phosphate (Ph_3PO_4) and especially TPP, which is molten under reaction conditions ($> 100^\circ\text{C}$) and solubilizes the catalyst efficiently. TPP acts as multi-purpose medium in providing effective dispersion of the Rh complex, in achieving high regioselectivities (high phosphine/Rh ratios) and in stabilizing the catalyst against deactivation. The most satisfactory catalysts were those containing at least 0.6 g TPP per gram of SiO_2 .

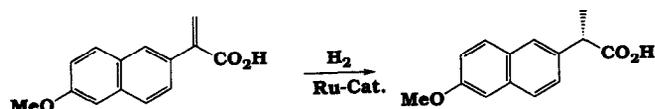
However, the use of this type of catalyst is limited to oxo synthesis in the gas phase. Substrates which are liquids under reaction conditions, for instance long chain olefins, solubilize the solvent layer and fast deactivation by

leaching is observed. These problems have been overcome partly by SAPC, where the solvent is water, which is immiscible with the substrate and product phase. Additionally, the loss of solvent under operating conditions leads to deactivation of the catalyst as the metal particles tend to agglomerate. In order to avoid this disadvantage the reaction gases have to be saturated with the adsorbed liquid. This problem was recently solved by application of a turbulent fluidized reactor bed [208].

The application of SLPC to the hydroformylation of propene [208] and allyl alcohol has been described. But in recent years, developments in this research area have waned. In 1987 it was announced that a general pre-design of a large-scale SLPC plant for the hydroformylation of propene had been completed [199]. Yet, to the best of our knowledge, this type of catalyst has not been commercialized up to now.

2.1.3.3.2.3. *Supported aqueous phase catalysts (SAPC)*. Supported aqueous phase catalysts have been reviewed recently [93,200]. Developed in 1989 by Davis and Hanson [201], these catalysts have been used for hydroformylation [202], hydrogenation [203] and Wacker oxidation of alkenes [204]. As a subspecies of SLPC, the SAPC were designed to convert liquid substrates that are completely insoluble in water, for instance long chain olefins, with water-soluble catalysts. Despite promising results, these catalysts will hardly be used in industrial applications. The activity of SAPC is strongly dependent on the water content of the solid particle. The optimum range is between 3 and 7 wt-%. Decreased activity is observed at higher or lower water-loadings and not due to metal loss through leaching. Crucial measurement and control of the water content are impossible during continuous operation modes. Additionally, the water-soluble ligands used, like TPPTS, are to some extent degraded under reaction conditions. This loss can not be compensated for by simply adding ligand. Last but not least, recovery of the expensive rhodium metal after the reaction is problematic and unsolved.

However, for expensive products, for instance in the pharmaceutical sector, the costs of a catalyst sometimes play no major role. SAPC made a valuable contribution to this field just recently. Davis showed that with the water-soluble Ru complex $[\text{Ru}(\text{BINAP-4SO}_3\text{Na})(\text{C}_6\text{H}_6)\text{Cl}]\text{Cl}$ immobilized in a thin film of ethylene glycol adsorbed on a controlled-pore glass support, 2-(6'-methoxy-2'-naphthyl) acrylic acid is asymmetrically hydrogenated to the anti-inflammatory agent naproxen [(Eq. 5)] with an ee of 96% [186,187]. Keys to this success were the application of ethylene glycol as a solvent and the synthesis of the sulfonated BINAP ligand [205]. Using water as a solvent, almost no chiral induction and only limited stability of the catalyst was observed. It remains to be seen what impact this result will have on hydroformylation with SAPC catalysts. Currently, they are being intensely studied in China [206] and recent developments of analytical methods provide more information on structure and mobility of the metal complex within the liquid film [207].



(5)

2.2. Special applications of hydroformylation

2.2.1. Special olefins

As compared to the conversion of propylene (world capacity approx. 4.5 million tons annually) the hydroformylation of higher olefins (annual output 1.5 million tons) is less important [11]. According to a recent survey conducted by Roeper most of the processes used for the conversion of higher molecular olefins are cobalt based processes with proven but costly techniques for Co separation and Co recycling [152] (b). On the other hand there are only a few developments based on Rhodium catalysts and olefins other than propylene (Mitsubishi [209,210], Ruhrchemie [211,212]). According to Fig. 6 biphasic processes for the hydroformylation of higher olefins (approx. $> \text{C}_3$) or functionally substituted olefins offer various advantages such as the simplification of reaction sequences and reduced expenditure on the catalyst cycle. So far the work on these biphasic processes for the processing of

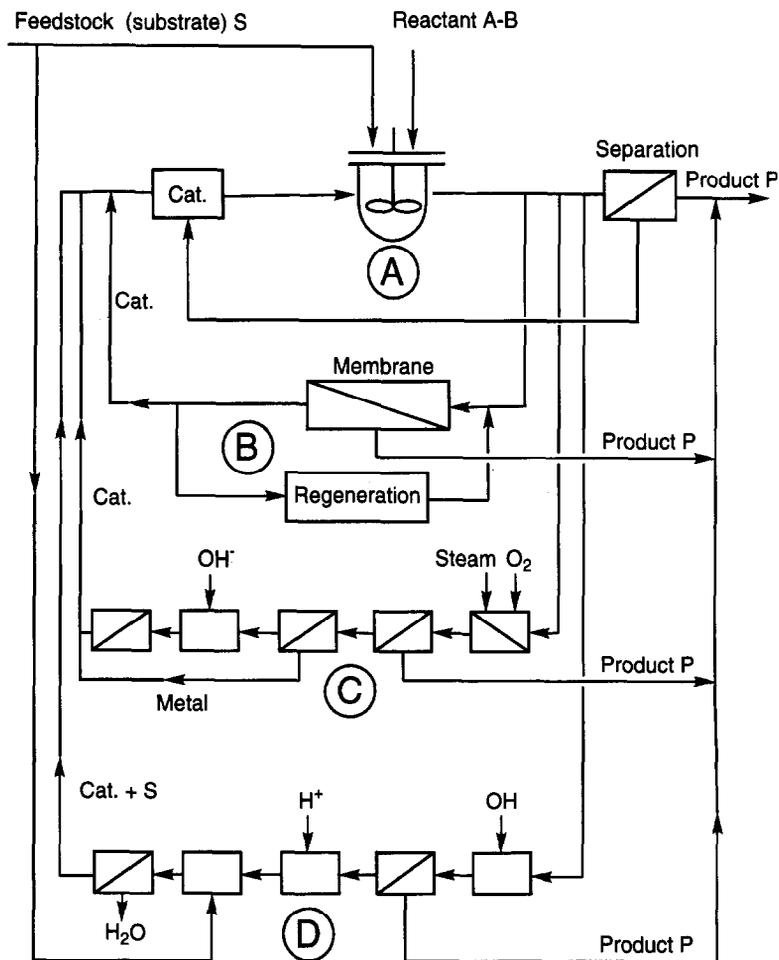


Fig. 6. Oxo-catalyst recycling steps: A = biphasic, B = membrane technique, C = thermal separation, D = chemical separation and recycle.

higher olefins has not been successfully realized on an industrial scale except for Kuraray's developments.

Already together with early work on biphasic oxo processes with ligand-modified Rh catalysts high-molecular olefins played a role (Wilkinson et al. [119] using triphenylphosphine monosulfonate, TPPMS; Kuntz at Rhône-Poulenc using the corresponding TPPTS [213]). Using these reactions among others as examples the early researchers found in comparison to the conversion of lower olefins very minor reaction rates apart from emulsifying surface-active properties of the ligands. The decreasing miscibility of the aqueous catalyst solutions with increasing C number of the higher olefins ought to be responsible for lowering the conversion rate. The following proposals should improve the solubilities and thus the conversion of biphasic processes:

1. Variation of the water-soluble ligands by means of surfactant or solubilizing properties
2. Addition of solvents and/or co-solvents
3. Other means to improve the miscibility and thus the solubility.

Often the ligand variation of biphasic processes performs a number of functions simultaneously: it enhances the solubility of the aqueous phase and influences electron donor properties; it increases the selectivity and improves the steric or electronic environment of the homogeneous catalyst (e.g. [59,121,137,214,215,243]). A link to solubility improving ingredients added externally are those water-dissolved ligands (like TPPTS), the hydrophilic substituents of which have been modified by quaternization [216–218]. According to an early work of Dror and

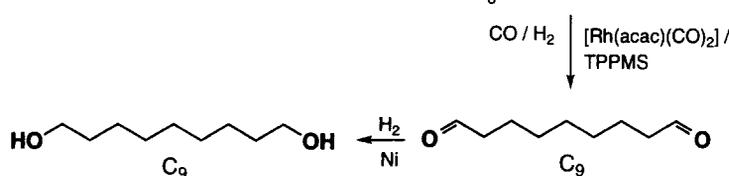
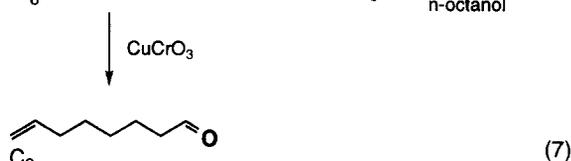
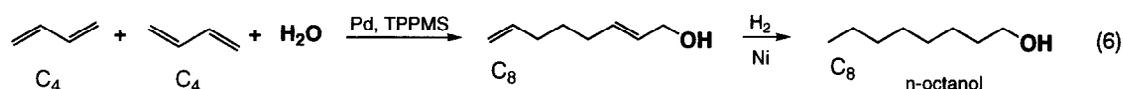
Manassen [219] proposals for compounds to increase the reciprocal solubility include cationic or non-ionic tensides (amphiphilic detergents) [220,221], covering other central atoms as well [222]. Complex catalysts with inherent surface-active attributes (surface-active phosphines) ought to act particularly elegant, i.e. compounds combining a suited electronic and steric environment as well as detergent properties [95,223,224]. According to Fell [223] the effect of these ligands is a consequence of a solubilization of the water-immiscible high molecular olefins, thus increasing the mass transport. The possibilities of detergents to aggregate and to form micelles ('micelle solubilization') might be helpful.

A relatively poor effect has been observed using solely solvents or co-solvents such as EtOH or BuOH as solubilizers [159–162]. This was discussed in Section 2.1.3.2. [162,163,225].

Intense research work has been conducted by Russel/Johnson Matthey to develop a biphasic oxo process for dodecene-1 as an example of higher olefins [220,226]. Favorable results could only be obtained when high concentrations of amphiphilic additives (additive: Rh ratios of 20:1) were used and therefore did not yield a good basis for a commercial (i.e. economical) process. Another approach to the use of P-bonded polyalkylene glycol ethers and their reverse 'cloud points' is described in Section 2.1.3.3.1.

There are only few proposals for the application of new techniques and processes for the conversion of higher molecular olefins or their functional substitutes. Exxon described an 'aldolizing oxo synthesis', a variant of the former Aldox process [227], including the conversion of higher olefins C_n to aldehydes C_{2n+2} in a one-step process consisting of hydroformylation and subsequent aldolization, followed by hydrogenation. Thus the valuable 'dimeric' plasticizer alcohols can be obtained using a biphasic procedure with diethylene glycol as second phase and with special ligands [228]. Union Carbide claimed an 'oxidative hydroformylation' for the direct conversion of olefins C_n to carboxylic acids C_{n+1} by using oxygen containing syngases [229]. Special ligands such as tri(*n*-octyl)phosphine oxide (TOPO) are essential, for example in the manufacture of propionic acid and its anhydride from ethylene.

Two biphasic developments of Kuraray Corp. are used industrially [cf. Eqs. 6 and 7]:



Using Kuraray know-how Arco produces butanediol-1,4 from allyl alcohol (which is manufactured via isomerization of propylene oxide) by a two-step process: the hydroformylation of allyl alcohol in the presence of Rh/phosphine catalysts and of sulfolane yields 4-hydroxybutanal, which in turn is hydrogenated to butanediol [230–232]. Alternatively *n*-octanol or nonanediol-1,9 may be produced by the telomerization ('hydrodimerization' according to earlier work done by Kuntz [233]) of butadiene and water. The reaction product of the first step is octa-2,7-diene-1-ol [234]. This conversion takes place in water/sulfolane mixtures and needs Pd complexes with water-soluble ligands (preferably TPPMS) and co-catalysts. The dieneol may be hydrogenated to *n*-octanol, which is a valuable plasticizer alcohol. Similar developments (but without technical realizations) have been described by BASF [235], Mitsubishi [236], and Shell [237].

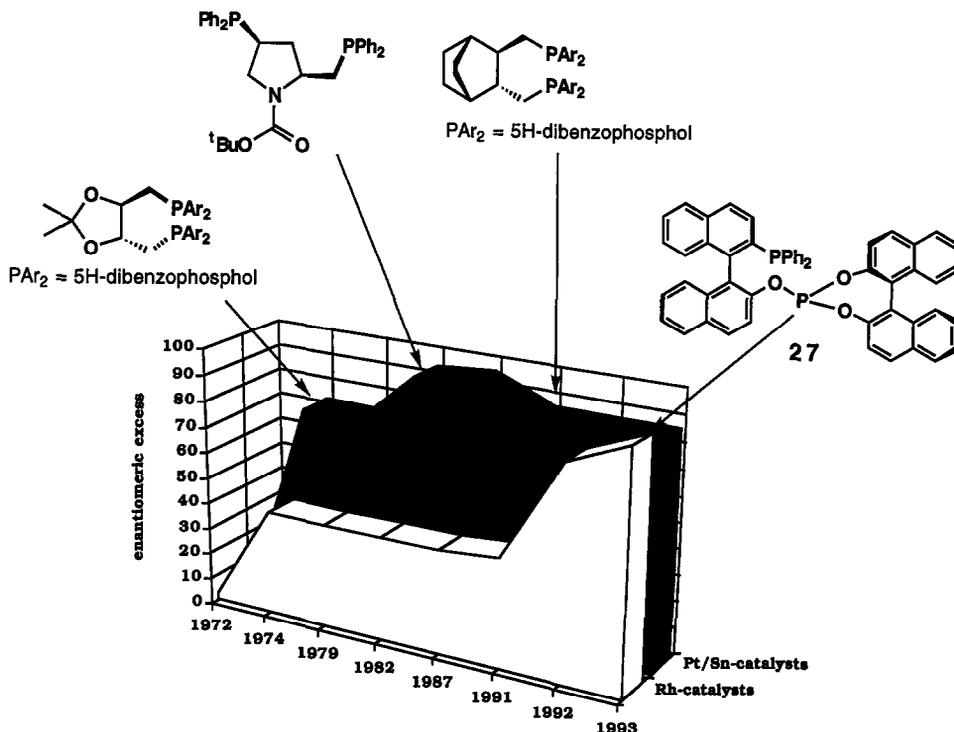


Fig. 7. Enantiomeric excesses in the hydroformylation of styrene and substituted styrene derivatives with Rh and Pt based catalysts (incl. ligand 27).

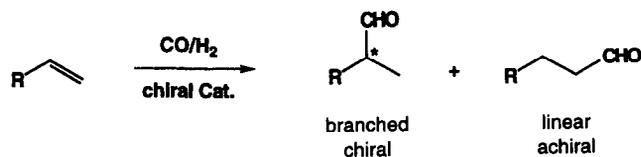
The dienol may be converted selectively via isomerizing reduction to the enal octa-7-en-1-al, which in turn is hydroformylated to nonanedial-1,9 and hydrogenated to nonandiol-1,9 [238]. Biphasic processes combined with extractions are used for this reaction sequence [93].

As to other oxo reactions of functional derivatives of olefins (acrylic acid or acrylic esters, poly-isobutenes, oleic alcohol, high molecular fatty acids etc.) cf. [152](b) [161,188,239–241].

According to a proposal of Horváth the problems arising from the limited reciprocal solubilities of water-phase and higher olefins should be overcome by application of the SAPC technique [242]. For other biphasic – but non-aqueous – processes cf. Section 2.1.3.3.1.

2.2.2. Asymmetric hydroformylation

The asymmetric hydroformylation reaction represents a versatile tool to produce a wide variety of chiral molecules. Those compounds are valuable precursors for pharmaceuticals and agro chemicals. The potential market for synthetic chiral products in bulk form at the beginning of the next century is estimated to be worth more than \$2 billion [244]. The basic problem in this particular reaction is to combine high regioselectivity with high enantioselectivity. In contrast to the goal of high linear-to-branched ratios in conventional hydroformylation, the desired product here is the branched compound with an asymmetric carbon atom as carrier of chirality [Eq. 8].



(8)

Table 2
Production capacities for aldehydes by hydroformylation^a

Region	Capacity (1000 t/year)					2-EH ^c
	C ₃	C ₄ ^b	C ₅ –C ₁₃	>C ₁₃	Σ	
Europe (western)	25	1,600	535	85	2,245	870
Europe (eastern)		785			785	450
North America	75	970	450	270	1,765	300
Latin America		120	55		175	150
Far East (including Australia)		1,040	140	30	1,210	650
Total	100	4,515	1,180	385	6,180 ^c	2,420
%	2	73	19	6	100	

^a Estimate, 1993.

^b Including i-butanal.

^c 2-EH: 2-ethylhexanol.

The status of asymmetric hydroformylation was recently summarized in a review by Botteghi [245] (a). The asymmetric variant of oxo synthesis was first applied in 1972 by researchers in Italy, Japan and at BASF in Germany [246]. Since those early days considerable progress has been made. As can be seen from Fig. 7, platinum–diphosphine catalysts modified by SnCl₂ performed the enantioselective hydroformylation of styrene and derivatives with high ee's at an early stage. However, those catalysts suffer from their low regio- and chemoselectivity. The moderately branched/linear ratios together with a high hydrogenation activity under hydroformylation conditions were detrimental to the commercialization of these catalysts.

Nowadays research in the area of asymmetric hydroformylation is heading towards rhodium catalysts, after Takaya [247] and Union Carbide [248] announced major breakthroughs with phosphine–phosphinite and diphosphite ligands, respectively. This ligand **27** gave ee's up to 95% in the hydroformylation of substituted styrene derivatives. The *i/n* ratios were higher than 86/14. Conversions are >99% at substrate/catalyst ratios of 300–2000 to 1. This outstanding catalyst has been patented widely [249].

Similar results were reported by Union Carbide with their diphosphinite ligand **28**. Under very moderate reaction conditions, room temperature and 35 atm syngas pressure, styrene was hydroformylated in toluene as a solvent with

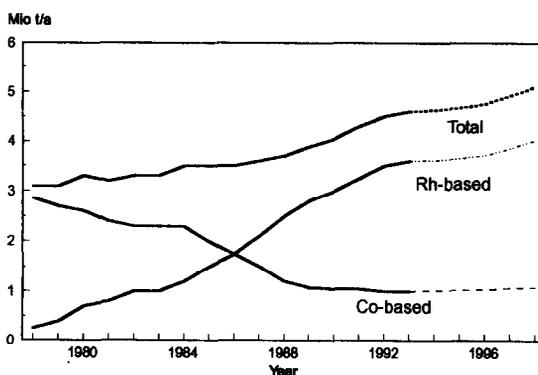
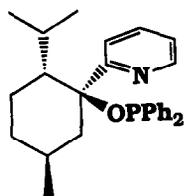
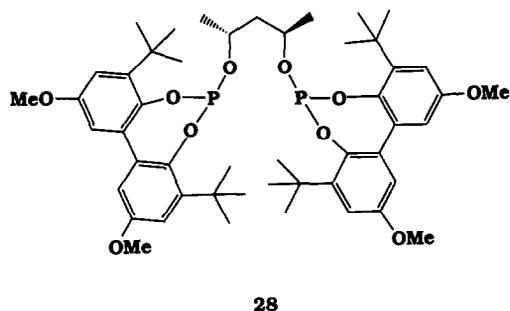


Fig. 8. Development of C₄ production capacities (estimate) [11].

up to 90% ee. An iso/n ratio of 50:1 was obtained at a ligand/rhodium ratio of 4:1. Yet the reaction rates are rather low ($0.11 \text{ g mol}^{-1} \cdot \text{h}^{-1}$).

Both developments opened up a new area of asymmetric hydroformylation. The results are very promising and research is focused on the basic ligand structures. Nevertheless, other ligands like the P–N ligand **29** also show very high selectivities (Scheme 13). Recently Faraone reported in the hydroformylation of vinyl naphthalene the exclusive formation of the branched aldehyde while using a rhodium/**29** catalyst (conversion of 100%) [250]. The ee obtained was 78% for the (*R*)-enantiomer. With methacrylates, ee's of 92% were observed.

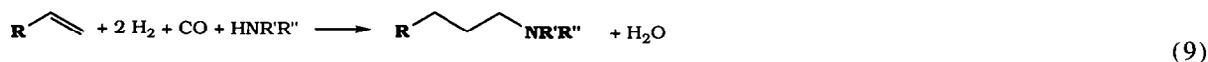


This brief discussion shows that research in asymmetric hydroformylation just recently received new impetus after many years of stagnation. Basic discoveries made in 1993 and 1994 were groundbreaking and now point the way towards future developments.

2.3. Special variants of hydroformylation

2.3.1. Aminomethylation

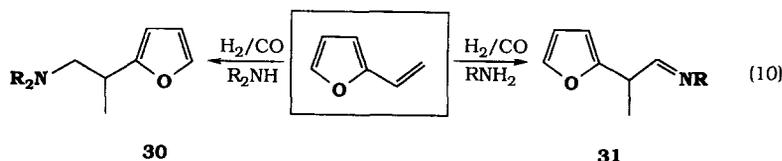
Condensation of aldehydes with primary or secondary amines yield imines and enamines respectively. Alkene hydroformylation and the condensation reaction can be performed in one step. This so-called aminomethylation (or hydroformamination) reaction originally discovered by Reppe in 1949 [251] is described by Eq. 9. The reaction proceeds via a three-step mechanism: hydroformylation, condensation and hydrogenation.



Originally catalyzed by iron pentacarbonyl, the reaction was limited to ethylene and propene and needed harsh conditions ($T > 150^\circ\text{C}$, $p = 150 \text{ atm}$). The other catalysts that were investigated comprise $\text{HRh}(\text{CO})(\text{TPP})_3$ [252], $\text{Rh}_6(\text{CO})_{16}$ and $\text{Ru}_3(\text{CO})_{12}$ [253]. Active catalyst precursors for the hydroformylation step catalyze the whole reaction most efficiently, indicating that the transformation of the alkene to the aldehyde is the crucial step. In 1984, catalytic amounts (20 mol-% cobalt) of $\text{Co}_2(\text{CO})_6(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ were successfully applied to the amino-

methylation of propylene with morpholine or piperidine as amines [254]. The *n*/iso distribution was similar to the hydroformylation of propene with Co-catalysts (66% linear isomer). Other by-products were formamides, butyraldehydes (branched and linear) and butyl alcohols.

Aminomethylation has been extended to produce tertiary polyamines as well. The polymers are synthesized by condensation of alkenes with secondary polyamines or by reaction of polyalkenes with primary or secondary amines. Recently, it was reported by Russian scientists that 2-vinylfuran is converted to compounds **30** and **31** by using $\text{HRh}(\text{CO})(\text{TPP})_3$ in up to 85% yield (Eq. 10) and structures **30** and **31**) [255].



Kalck demonstrated in 1992, that aminomethylation of 1-octene with diethylamine to yield *N,N*-diethylnonylamine is performed by $\text{Rh}_2(\mu\text{-S-}^t\text{Bu})_2(\text{CO})_2(\text{TPP})_2$ in THF [256]. Conversion of the olefin is >98% and amines are formed in 80% yield with a selectivity of 98% to the linear product. The reaction was performed at moderate conditions and was very sensitive to the solvent used. For instance in dichloroethane, extensive polymerization was observed. Other amines like morpholine, diisopropylamine or *n*-butylamine gave lower rates and selectivities. However, the overall results are promising and it remains to be seen whether the commercialization of this reaction will be possible in the coming decades.

2.3.2. Homologation of carboxylic acids

In the late seventies and early eighties the homologation of carboxylic acids by syngas according to Eq. 11 was investigated in some detail. The majority of $\text{C}_2\text{--C}_6$ carboxylic acids are generated by methanol carbonylation, butane or acetaldehyde oxidation, hydroformylation/oxidation and fat splitting/fractionation. Additionally, Eq. 11 would give access to completely syngas-based higher acids, as methanol is made from syngas and converted to acetic acid by carbonylation.



Knifton published the carbonylation (homologation) of acetic acid with syngas by homogeneous Ru or Rh catalysts [257]. With iodide promoters like methyl iodide or caesium iodide Ru catalysts (RuO_2 , $\text{Ru}(\text{acac})_3$, $\text{RuCl}_2(\text{TPP})_2$) gave acetic acid conversions up to 70%. The ratios of propionic:butyric:valeric acid were roughly 30:8:1. Rh catalysts like $\text{Rh}(\text{acac})_3$, Rh_2O_3 or RhCl_3 were more selective in the formation of propionic acid (ratios 70:20:1) but showed lower conversion rates (<54%). However, the overall efficiency of this reaction is too small to be competitive with the aforementioned well-established processes.

The reaction of carbon monoxide with HI to yield acetic acid has been reported by Kaplan [258]. The amount of product is very small. However, it was observed that the acetic acid reacts further with CO to generate propionic acid, a homologation reaction similar to Knifton's work. The homologation of methyl and C_n formates [259] and methyl esters of propionic, butyric, valeric, isobutyric and pivalic acids was reported by Jenner [260]. Mixtures of Co acetate, Ru acetylacetonate and iodide promoters were used to perform the reaction at 200°C and 290 atm of syngas pressure. Methane, CO_2 , acetaldehyde, methanol and ethanol were formed very unselectively apart from the free acids and ethyl esters thereof. A cooperative effect of Co and Ru has been observed, the optimum Co/Ru ratio being 0.4. The results clearly indicate the selectivity problems in homologation reaction, which are still unsolved [261].

2.3.3. Miscellaneous reactions

Quite a number of catalytic reactions related to hydroformylation have been reported. Hydrogenation of carbon monoxide [262], homologation of alcohols [263], silylformylation of alkynes and propargyl alcohols [264] have been studied extensively and are not considered further here. Specific carbonylation reactions like alkoxycarbonylation, hydroxycarbonylation and related reaction will be discussed in Section 3.

2.4. Technical developments in hydroformylation

2.4.1. General remarks

Over the past 15 years steady and continuous growth in the production capacity of aldehydes by the hydroformylation reaction has taken place. Table 2 shows the estimated capacities for aldehydes generated by hydroformylation of ethylene, propylene and higher olefins, along with their regional distribution [11].

Accounting for a share of about 73% of total production capacity, C₄ products have firmly established their leading position in this field. Ethylene hydroformylation to propanal amounts to 2–3% of the hydroformylation capacity for C₄ products and is only of minor importance. The hydroformylation of olefins of medium chain length, predominantly in the C₈/C₉ range (di-isobutylene, propylene trimer), makes up around 20% of the total production capacity. Only about 6% of the total production capacity is used to hydroformylate higher olefins. The individual shares of the three main product groups and the regional distribution are given in Table 2.

Table 2 further outlines the estimated capacities for 2-ethylhexanol (2-EH) production. In total, about 60% of C₄ capacity (or about 70% of the n-butanal capacity) is required to produce 2-EH. However, regional deviations between C₄/2-EH capacities are obvious, indicating that n-butanal is to be considered a commodity with worldwide availability. Bearing in mind that both 2-EH and the C₉/C₁₀ alcohols are nearly quantitatively absorbed in plasticizer production, the enormous significance of hydroformylation for the polymer industry, especially for PVC, is underlined. In contrast to repeatedly published predictions, a decrease in the application of 2-EH as plasticizer alcohol has not been observed to date.

Rhodium-based processes dominate in the hydroformylation of propylene. On the other hand, the production capacity of cobalt-based processes has remained at a virtually constant level in the C₄ field over the past years (see Fig. 8).

Several reasons may be taken into account for what only has been a small decrease in importance: an existing high-pressure infrastructure which is also used for the hydroformylation of olefins higher than propene, where cobalt-based processes are advantageous; a combined cobalt recovery and recycling system for the hydroformylation of different olefins, and the use of tail gases from low pressure hydroformylation units.

A completely reverse situation is encountered in the field of hydroformylation of olefins other than propylene (Table 3): cobalt dominates rhodium by far, the 9:1 ratio being in favour of cobalt. One reason is the low reactivity of rhodium in case of branched olefins with partially internal carbon double bonds, the high boiling points of the product aldehydes is the second, as too much thermal strain is imposed onto the catalyst during product separation by distillation.

Looking at the hydroformylation of propylene, the technology of the cobalt catalyzed processes has remained basically unchanged over the years, whereas the introduction of rhodium as catalyst has founded a new generation of hydroformylation processes, as can be seen from Table 4.

The rapid ascent of rhodium-based low-pressure oxo processes (LPO processes) was favoured by a number of frequently cited advantages: mild reaction conditions, simpler and therefore cheaper equipment, high efficiency, high yield of normal products and easy recovery of the catalyst.

However, an even more decisive development was the rise in the propylene prices which started with the first oil supply crisis in 1973 and led to a remarkable shift in the cost structure of butyraldehyde manufacturing in years that followed. The increase in the price of the raw material was paralleled by an increase in the cost of energy. With respect to raw material utilization and energy conservation, the LPO processes were more advantageous than the cobalt technology (depending on the credit for iso products), thus leading to their rapid growth.

Table 3
Capacities for oxo products by processes (without C₄ products, 2-EH)

Process		1,000 t/year	%
Exxon	(Co)	500	30
Shell	(Co)	400	24
CdF Chimie	(Co)	350	20
Nissan	(Co)	130	8
BASF	(Co)	100	6
UCC	(Rh)	100	6
Hoechst Celanese	(Rh)	40	2
Mitsubishi Kasei	(Rh)	30	2
BASF	(Rh)	30	2
Sub total		1,680	100
Unknown		0	
Total		1,680	

Besides their high specific activity, the pronounced thermal stability of rhodium–phosphine complexes, even in the absence of carbon monoxide, influenced the technology of the first generation of LPO processes. The basic idea was to retain the catalyst in the synthesis reactor and to separate catalyst and butyraldehydes by distillation under reaction conditions. Two requirements had to be fulfilled: a high boiling solvent for the catalyst and the excess of ligand had to be found, and a sufficient amount of gas had to be passed through the reactor to entrain the butyraldehydes. Condensation products of butyraldehydes, i.e. the heavy ends formed anyway in the process, turned out to be an appropriate, cheap and readily available solvent [265], thus covering one requirement. The solution to the other one proved unsatisfactory: a huge gas recycle was necessary to remove the butyraldehydes from the reaction zone (gas recycle process) to keep the level of liquid inside the reactor constant, which is energy-consuming and markedly complicates the overall process.

Nevertheless, in comparison to the cobalt technology even the first generation of LPO processes proved successful and was promoted by a number of companies (e.g. Celanese, Union Carbide, BASF, Mitsubishi) mostly in parallel. One of the first plants for butyraldehyde production belonged to Celanese [14] (b) (now Hoechst Celanese), tightly followed by Union Carbide/Davy Powergas/Johnson Matthey and other companies.

Later on, the efficiency of the *gas* recycle process was improved by a switch-over to the *liquid* recycle process, to which most plants have been converted in the meantime. Catalyst solution and aldehyde products leave the reactor

Table 4
Comparison of cobalt and rhodium based processes

Catalyst	Cobalt (classical) HCo(CO) ₄	Rhodium (ligand modified) HRh(CO)L ₃
Temperature [°C]	130–190	85–130
Pressure [bar]	200–300	12–50
Metal concentration [% b.w.]	0.1–0.5	0.01–0.05
LHSV [h ⁻¹]	0.5–1.5	0.1–0.3
n/i ratio	80/20	> 90/10
Formation of by products	high	low
Catalyst recovery and recycle	complicated	simple

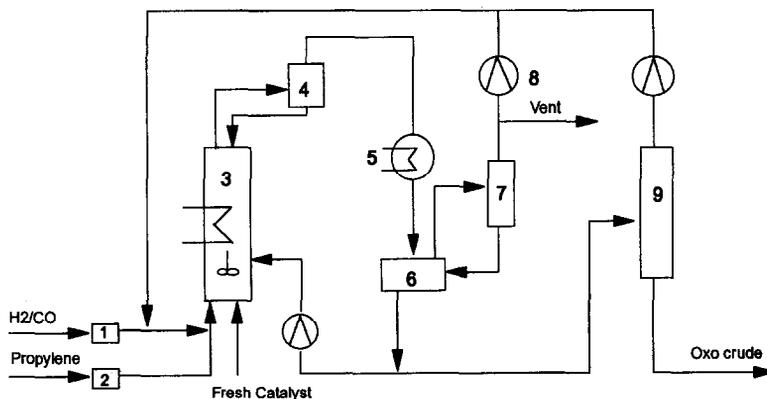


Fig. 9. UCC process: Gas recycle [280].

as liquid and are separated outside in several stages of thermal operation, which finally lead to raw aldehyde, catalyst solution and a combined stream of gas, the latter two being recycled to the reactor. Despite the improvement with respect to the former gas recycle, the liquid recycle also demands a relatively complicated separation of products from catalyst.

A far more elegant solution was the one offered by the Ruhrchemie/Rhône-Poulenc (RCH/RP) process, which was established in 1984 on an industrial scale: three-fold in *meta*-position sulfonated triphenylphosphine (TPPTS, as sodium salt) as the ligand yields the water-soluble catalyst $\text{HRh}(\text{CO})(\text{TPPTS})_3$. Because of the mutual insolubility, the separation of the aqueous catalyst phase and the butyraldehydes was extremely simplified, circumventing all the common difficulties and leading to very efficient operation (cf. Section 2.1.3.2.).

2.4.2. Today's oxo processes

2.4.2.1. UCC process

In 1971 a joint development program was started by Union Carbide Corp. (UCC), Johnson Matthey and Co and the former Davy Powergas Ltd. (today Davy McKee) to develop and commercialize a process using a Rh-containing homogeneous catalyst to carry out hydroformylation [266]. Research work on Rh catalysts had been underway in US since the mid-1960's, but about 10 years of research and process development were needed before until the first butyraldehyde plant came on stream in 1976 at Ponce, Puerto Rico [267]. The engineering was performed by Davy Powergas and the catalyst was supplied by Johnson Matthey and Co. At about the same time as UCC, Wilkinson at the Imperial College in London developed a similar catalyst system. Patents in this area were assigned to Johnson Matthey and Co [268].

In commercial applications of propylene hydroformylation the process underwent several modifications predominantly aimed at improvements in the product/catalyst separation. The very first process version, which was later on named the *gas recycle process*, effected the removal of the product aldehydes [269–271] from the catalyst solution by applying a large gas recycle in order to evaporate the aldehydes. The catalyst solution consisted of high-boiling aldehyde condensation products (dimers, trimers and various other aldehyde consecutive products), in which an excess of TPP and the Rh complex itself was dissolved [272,273]. In order to keep the volume of this reaction mixture constant, the conditions (temperature [95°C], partial pressures, total pressure [15–18 bar] and gas flux) had to be maintained in a manner which allowed continuous evaporation of the aldehyde products generated by the hydroformylation reaction [274]. These requirements led to a fairly complex plant equipment design (Fig. 9).

Propylene and make-up synthesis gas are carefully purified (1, 2) and, together with recycle gas, are introduced into the stainless steel reactor (3) via a sparger. The stirred reactor is equipped with an external heating jacket (for start-up) and internal cooling coils. Vaporous product effluent passes demisting pads (4) to prevent carry-over of catalyst and liquid products. Part of the gaseous aldehyde is condensed in a cooler (5) and collected in a separator

Table 5
LPO process: typical data [280]

Composition of product streams				
Product	Liquid	Reactor		Raw aldehyde [% b.w.]
		in [mol-%]	out [mol-%]	
iso-Butyraldehyde	35 ^a	0.3	1.0	7.14
n-Butyraldehyde		1.8	8.8	82.56
Carbon dioxide		1.2	1.2	0.39
Propane		14.3	14.6	4.40
Propylene		20.5	14.9	4.82
Carbon monoxide		9.9	4.7	0.06
Methane		3.7	3.9	0.08
Hydrogen		48.3	50.9	0.01
Rh (ppm)	275			
TPP (% b.w.)	7,5			
Trimer aldehydes (% b.w.)	50			
Higher condensates (% b.w.)	7,5			

^a iso-Butyraldehyde and n-butyraldehyde together.

(6), from which the recycle gas leaves via demister (7) to the recycle compressor (8). A slip stream is taken to the vent. Part of the condensed aldehyde from separator (6) is recycled to the reactor to keep the level of liquid constant. The main stream of crude oxo products is sent to the upgrading section [275].

The liquid catalyst solution contains about 35% b.w. of aldehydes (Table 5). In order to keep the volume of liquid in the reactor constant it is necessary to carefully control several variables: reaction and condensation temperature, amount and composition of recycle gas, input of propylene and synthesis gas. For stable operation a high volume of recycle gas has to be supplied: about 4.5 N m³ per kg of aldehydes generated, an energy consuming procedure. The productivity is 2–4 mol aldehyde/catalyst volume · h, the selectivity towards aldehydes 93%.

In order to avoid these drawbacks and following RCH/RP's excellent experiences with liquid recycles, the gas recycle was replaced by the *liquid recycle variant* (Fig. 10) which is in use in most modern LPO plants. Combinations of gas and liquid recycle have also been described, claiming increased propylene conversion [276,277].

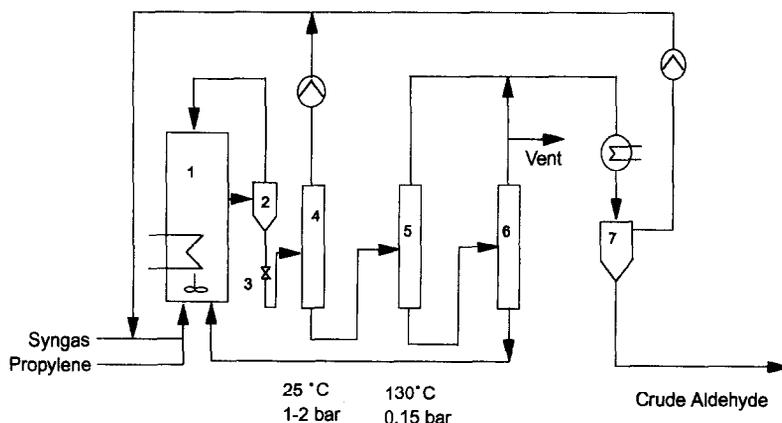


Fig. 10. UCC process: Liquid recycle.

Table 6
Liquid recycle: Typical data [277]

Temperature [°C]	85–90
Pressure [bar]:	18
Rh concentration [ppm]:	240–270
TPP [% b.w.]:	11–12
H ₂ /CO ratio:	1.07
Conversion propylene [%]:	85–89
Productivity [mol/l·h]:	1.5–2.0

The synthesis section was simplified: A stainless steel reactor (1) is provided with a sparger through which synthesis gas and propylene are introduced via a feed line together with recycle gas. The reactor is further equipped with an impeller for mixing and an internal or external cooler to control the reaction temperature. The catalyst is dissolved in high-boiling aldehyde condensation products. A liquid effluent stream is taken from the reactor at a rate sufficient to keep a constant level of liquid in the reactor. Besides dissolved gases this liquid stream contains aldehydes, the rhodium–phosphine complex catalyst, free phosphine ligand and higher boiling aldehyde condensation products. The splitting of this complex mixture requires several steps.

The liquid stream passes a separator (2), a let-down valve (3) for pressure release, and enters a flash evaporator (4) where the major part of inerts and unconverted reactants is taken overhead. The flashed-off gases are compressed and returned to the reactor, whereas the liquid is heated and fed to a first distillation column (5), from which vaporized aldehydes are taken as head stream. As the bottoms still contain aldehydes, a second distillation column (6) with sub-atmospheric pressure is required to concentrate the catalyst solution. The vaporous aldehydes from both units are condensed and sent to the upgrading section, the separated gases (7) are recycled (after compression) or vented. In order to limit a build-up of inert substances in the recycled gas streams and to reduce losses by venting, a separate treatment may be applied, e.g. an extraction of propylene by aldehyde products in the first and a stripping by synthesis gas in the second step [278,279]. Although raw material utilisation is improved by such a procedure, it contributes to the complexity of the catalyst and product separation section, which is the crucial part of both UCC processes. The performances of the UCC variants are given in Table 5 and Table 6.

2.4.2.2. Ruhrchemie/Rhône-Poulenc (RCH/RP) process

The idea of E. Kuntz (Rhône-Poulenc) to apply water-soluble rhodium complexes as catalysts for the hydroformylation reaction [125] was taken up and commercialized by Ruhrchemie AG for the hydroformylation of propylene. After only two years of development on the laboratory scale the first plant was erected in 1984 followed by rapid further increases in capacity to more than 300,000 t/year today [133].

The RCH/RP unit [21] (b) is essentially a continuous stirred tank reactor, followed by a phase separator and a strip column (Fig. 11). Reactor (1), which contains the aqueous catalyst, is fed with propylene and syngas. The crude aldehyde product passes into decanter (2), where it is degassed and separated into the aqueous catalyst solution and the organic aldehyde phase. The catalyst solution moves to heat exchanger (3) and produces process steam. Water lost in the aqueous phase can be replaced at (3), after which it returns to reactor (1).

The organic phase, containing the raw aldehyde, then passes the stripping column (4). Here the mixture is treated with fresh syngas, which acts as the counter-current stripping agent to move unreacted olefin back to reactor (1). Because there is no catalyst in the stripping column, no side reactions occur to decrease the selectivity or yield of the aldehyde. After this, the raw aldehyde is fractionally distilled into *n*- and *iso*-butanal in a conventional aldehyde distillation unit (5). The reboiler of this *n*/*iso*-column is a falling film evaporator incorporated in reactor (1). The heat of the oxo reaction is thus recovered as the reboiler heat source for the *n*/*iso*-column. This is an advantage over the classical oxo processes, which simply discard the oxo reaction heat. The RCH/RP process is a net steam exporter. The catalyst in fact remains ‘immobilized’ in the reaction system with rhodium losses < 10⁻⁹ g Rh/kg *n*-

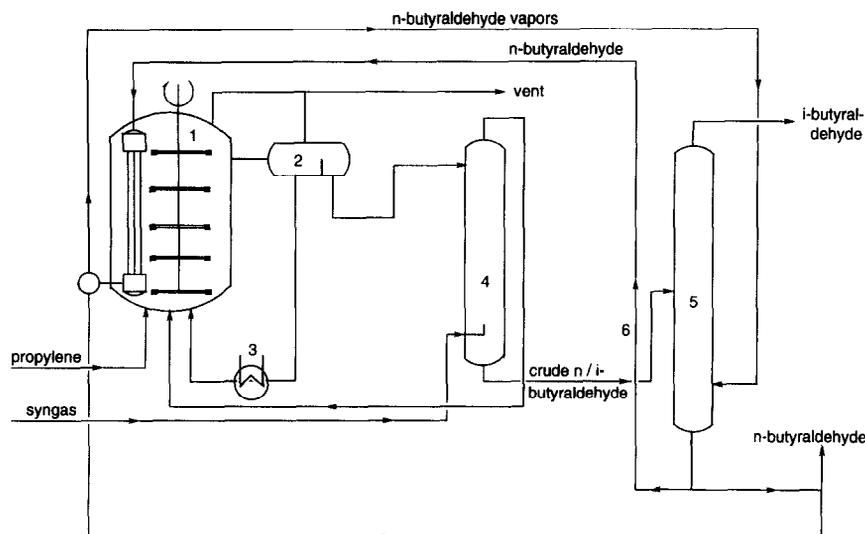


Fig. 11. RCH/RP's oxo process [21].

butyraldehyde. The use of water as solvent for the catalyst adds an further advantage to the process with respect to ecotoxicological considerations (Table 7).

The RCH/RP catalyst is not sensitive to sulfur or other oxo poisons that may enter with the feeds. The withdrawal of organic and other by-products with the organic phase and in the vent stream from decanter 2 prevents the accumulation of activity-decreasing poisons in the catalyst solution.

2.4.2.3. BASF process

Developed nearly in parallel to UCC's LPO process, the BASF process (Table 8) also makes use of a gas recycle to separate aldehydes and catalyst solution [281]. The latter also consists of aldehyde condensation products [282] with TPP and the corresponding Rh complex dissolved therein. With about 3–5% b.w. the concentration of TPP is

Table 7

RCH/RP Process: typical data [21] (b)

	Range	Typical
<i>Reaction conditions</i>		
Temperature [°]	110-130	120
Pressure [bar]	40-60	50
CO/H ₂ ratio	0.98-103	1.01
Aqueous/Organic phase	4-9	6
Propylene conversion [%]	85-99	95
Propylene quality [%]	85-99.9	95
<i>Product composition</i>		
iso-Butyraldehyde [% b.w.]	4-8	4.5
n-Butyraldehyde [% b.w.]	95-91	94.5
iso-Butanal [% b.w.]	<0.1	<0.1
iso-Butanol [% b.w.]	0.5	0.5
Butylformates [% b.w.]	traces	traces
Heavy ends [% b.w.]	0.2-0.8	0.4
n/i ratio	93/7-97/3	95/5
Selectivity to C ₄ products [% b.w.]	>99	>99.5
Selectivity to C ₄ aldehydes [% b.w.]	99	99

Table 8
BASF-process: typical data [284]

Reactor volume	135 m ³
Liquid volume	ca. 2/3 of reactor volume
Propylene in	4,000–4,400 kg/h
Butyraldehydes out	5,700–6,500 kg/h
Propylene conversion	84–86%
n/i ratio	84/16
Rhodium concentration	160–190 ppm
Gas recycle	18,000–26,000 N m ³ /h
Productivity	0.063–0.072 kg/l·h
TPP concentration	3,5–4,5% b.w.
TPP/Rh	ca. 100/1 mol/gAt.
Temperature	ca. 110°C
Pressure	ca. 16 bar
Propane formation	ca. 2% of propylene converted
High boiling products	ca. 0.5% of propylene converted
<i>Partial pressures</i>	
propylene	4.8 bar
carbon monoxide	0.6 bar
hydrogen	8.0 bar

rather low, thus limiting the rhodium concentration to a level below 200 ppm in order to establish a P/Rh ratio of about 100/1 (mol/g at.). Accordingly, the n/i ratio is somewhere in the range of 84/16. With a temperature of about 110°C the pressure is limited to 15–17 bar to avoid too large a recycle.

The process scheme corresponds to the gas recycle process already described. Propylene and synthesis gas (H₂/CO = 55/45) are fed to a stainless steel tank reactor with intense mixing. Aldehydes are withdrawn by a recycle gas stream, condensed by partial cooling and freed from dissolved gases in a stabilizer column [283]. The combined gaseous streams from these operations are recompressed and sent to the reactor. A vent stream is used to control the level of propane in the gas loop. Due to the application of the recycle, the syngas actually entering the reactor is extremely rich in H₂ (Table 8).

2.4.2.4. Exxon process

Designed and applied for the hydroformylation of olefins in the C₆–C₁₂ range, the Exxon process is representative of a cobalt catalyst recycle without change of the oxidation or coordination state of the catalyst metal. This is in contrast to the processes in which the removal of the catalyst after hydroformylation is achieved by oxidation with e.g. air/acetic acid (older BASF process) or by thermal degradation of the cobalt carbonyl (older Ruhrchemie process; cf. Fig. 6). In the Exxon process the so-called Kuhlmann (Produits Chimiques Ugine Kuhlmann, acquired by Exxon) catalyst cycle technology is applied, involving two main process steps: the recovery of sodium cobalt carbonylate and its regenerative conversion into cobalt carbonyl hydride. Obviously the older Kuhlmann technology has been refined and extended in some points, especially to increase the yields of valuable products and to reduce cobalt losses in the catalyst recycle.

Cobalt enters the process via a carbonyl generator and is fed into the oxo reactor together with the olefin stream, which already carries the recycled HCo(CO)₄ from an extractor. Together with purified syngas hydroformylation takes place under the usual conditions (160–190°C; 250–300 bar; 0.1–0.5% Co) in a reactor equipped with an external loop. After passing a separator, the crude product is treated with dilute aqueous caustic (e.g. 9–15% b.w. of reaction product as 3–5% b.w. NaOH) still under temperature and pressure to extract NaCo(CO)₄ as aqueous solution. A cobalt-free organic phase results after scrubbing with water. By addition of H₂SO₄ in the presence of syngas, HCo(CO)₄ is generated, extracted by an olefin stream and sent to the hydroformylation zone. Instead of the olefin as extractant other suitable compounds may be applied (e.g. hexanol).

Table 9
Exxon process: typical data [288,289]

Temperature [°C]	175
Pressure [bar]	290-300
H ₂ /CO ratio	1.16/1
Feed	Propylene trimer
LHSV [h ⁻¹]	0.7
Co-concentration [% b.w. of feed]	0.3
<i>Product composition [% b.w.]</i>	
Light products	11-13
C ₁₀ -aldehydes	72-74
Heavy ends	13-17

The reclaim of cobalt as described is not complete as some formation of Co²⁺ by oxidation cannot be avoided, leading to deterioration of the waste-water stream. For cobalt recovery from this stream, the usual techniques of precipitation may be applied, leading to carbonate or hydroxide. The overall losses are compensated by fresh cobalt, introduced by the carbonyl generator. In order to convert Co formate into HCo(CO)₄, the presence of palladium on carrier as catalyst is recommended.

The engineering of the Exxon process is beneficial because the catalyst does not undergo decomposition and is introduced in its most active and effective form. However, all the stages of catalyst separation and recycle have to be carried out under CO pressure, a requirement which may be considered as disadvantageous.

The product slate (Table 9) corresponds to the usual picture for cobalt hydroformylation. A number of proposals have been put forward to make use of the high boiling moiety of the raw oxo product.

2.4.2.5. Other processes

Despite a considerable number of publications and patent applications dealing with hydroformylation technology, comparatively few processes have successfully been commercialized besides those which have already been mentioned in the foregoing part. Two processes have gained commercial importance.

Back in 1974 Celanese (Hoechst–Celanese today) started the production of butyraldehydes by a process [285] which closely resembles the LPO process subsequently (1976) introduced by UCC. It is an open question which of the two companies was the really first to introduce low-pressure hydroformylation, as UCC claims to have run an ethylene hydroformylation unit at Ponce before the start-up of the propylene unit at the same site [14] (b) [286]. If any, there are only minor differences between the Celanese and the UCC process.

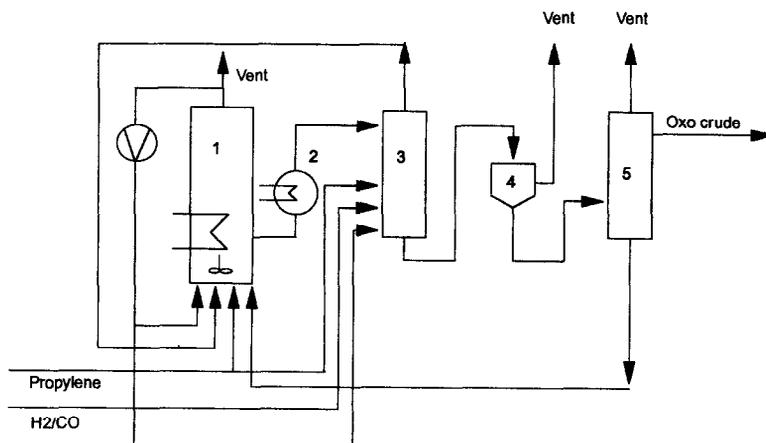


Fig. 12. Mitsubishi process.

Mitsubishi also operates a LPP for propylene hydroformylation [67] (a) [287] which comprises several features of common technology. As outlined in Fig. 12, the liquid mixture of aldehydes and high-boiling condensation products from reactor (1) passes a heater/cooler (2) and enters the top of the strip column (3). The gas recycle together with fresh propylene and synthesis gas is used to remove dissolved gases from the liquid effluent, which enters the gas-liquid separator (4) and then a distillation column (5) to separate aldehydes and the catalyst solution. Catalyst and strip gases return to the reactor entrance. The process can be considered a combination of gas and liquid recycle with a strip column. The following reaction conditions are stated to be typical: Temperature ca. 100°C, pressure 15–18 bar; Rh conc. 300–350 ppm, TPP concentration 20–22% and H₂/CO ratio approx. 1.015/1.

2.4.3. Special developments

Several attempts have been published to solve the problem of the separation of catalyst and products by immobilizing the catalytically active species on fixed supports (see Section 2.1.3.3.2.). So far, none of these developments has achieved technical realization, mainly because of insufficient long-term stability. For the liquid phase application, the fixation of rhodium to ion exchange resins, polymers with incorporated ligands or simply to oxidic carriers proved to be insufficient, and losses by leaching could not be conveniently suppressed. In gas phase operation, where rhodium was either dissolved in an excess of the molten phosphine ligand or in an aqueous solution of the ligand, the immobilizing phase was swept out by the time on-stream, carried by the gas flow as in chromatography, supported by the exothermicity of the hydroformylation reaction. In spite of the obvious advantages of fixed-bed operation, no acceptable solution has yet been presented.

Mitsubishi uses a modification of the Rh-catalyzed high-pressure hydroformylation of long-chain olefins like octenes or nonenes [88]. Hydroformylation is carried out in the presence of the weakly complexing triphenylphosphine oxide (TPPO) as ligand at pressures up to 200 bar. It is claimed that the activity of rhodium is diminished less by TPPO than by TPP, thus reducing the rhodium inventory in comparison to TPP as ligand. Before distillation of the nonanals or decanals, TPP is added to stabilize rhodium, the TPP being oxidized to TPPO before re-use of the catalyst solution by a non-disclosed oxidation procedure. Part of the catalyst solution is purged for external upgrading (cf. Section 2.1.2.3.).

2.4.4. Future aspects

The hydroformylation processes applied industrially have reached a high degree of maturity. Designed for the production of commodity chemicals, they have undergone subsequent improvement and have been in use for at least a decade and often much longer (cobalt-based processes). Accordingly, their production cost structure is mainly governed by raw material and capital costs and little room is left for improvements by process modifications. This fact is reflected by recent patent literature: no really significant alteration of the common hydroformylation technology has been published since the appearance of the RCH/RP process at the beginning of the eighties [129].

However, the question arises as to whether the principle of biphasic homogeneous catalysis with its obvious advantages in some fields has already arrived at its final state of development or if expansion is still possible and technically and economically justified. The driving force of further work in this area is the result of a general fault of established LPO processes: increasing difficulties arise with increasing chain length of the olefin which prevent their application for olefins with carbon numbers above C₆–C₇. These difficulties are either related to the increasing boiling point of the product, leading to problems in separation of the catalyst solution in the case of monophasic systems, or to low solubility of the olefins in the aqueous catalyst phase, the reason for the limitation in productivity with biphasic systems. The separation of catalyst and products by distillation can only be applied successfully within the limits of the thermal stability of the Rh catalyst complex, whereas the phase-separation technique has no restrictions in this respect. These facts lead to the conclusion that an extension of the two-phase principle offers per se the better chances for a general application in hydroformylation.

Some promising steps have already been undertaken and are discussed in Sections 2.2. and 2.3.

3. Carbonylation

3.1. New developments

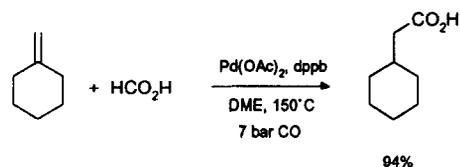
Carbon–carbon bond-forming reactions are the underlying fundamental principle of synthetic organic chemistry. Despite an explosion of new methods and reagents in all areas derivatives of carbonyl compounds are among the most versatile groups for further transformations. Today the functionalization of organic molecules with carbon monoxide to carbonyl compounds, in addition to hydroformylation, is an area that is rapidly growing mainly for laboratory-scale synthesis. On the other hand new applications of carbon monoxide in the synthesis of fine chemicals were very rare until the 80's. Because of the development of new reagents and deeper mechanistic understanding, fine chemical synthesis based on carbon monoxide is expected to grow in future.

Substrates for carbonylation reactions may be olefins, alkynes, and reactive aryl, vinyl or alkyl species. A number of reviews and monographs in this area have appeared since 1980 [290]. In the following section *new* applications of transition metal-catalyzed reactions will be discussed. Emphasis has been given especially to the development of new synthetic methods and to new commercial processes.

3.1.1. Carbonylation of olefins

3.1.1.1. Hydrocarboxylations and related reactions

Catalytic hydrocarboxylation and hydroesterification of alkenes have attracted considerable interest during the last 15 years. Co, Pd, Pt, Ni, Rh, and Ru have been used as catalyst metals. Main synthetic interest focuses on the development of superior regioselective methods. For reasons of working at milder reaction conditions (20–80°C, 1–10 bar CO) Pd and Rh catalysts were applied most frequently [291]. A recent example employed Pd acetate immobilized on montmorillonite in the presence of TPP and an acid promoter for the hydroesterification of aryl olefins. The reaction is totally regioselective for the branched isomer of aromatic olefins, while aliphatic olefins afforded branched chain esters only regioselectively with $n/i = 1/3$ [292]. On the other hand selective hydrocarboxylations to give linear acid derivatives have been described with Pd acetate and 1,4-bis(diphenylphosphino)butane (dppb) in the presence of formic acid [293] (Eq. 12), or Pd on carbon in the presence of dppb and formic or oxalic acid [294].



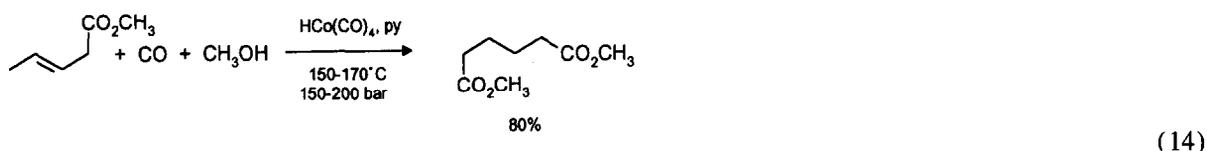
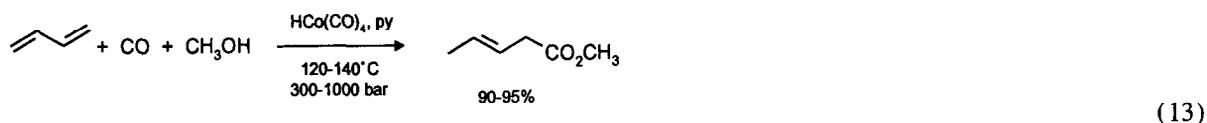
(12)

Moreover, the regioselectivity of the hydroesterification of alkyl acrylates catalyzed by $[\text{PdCl}_2\text{L}_2]$ complexes (L = phosphine ligand) could be largely controlled by variation of the ligands. TPP promotes preferential carboxylation to the branched isomer, whereas with bidentate phosphines the linear product is overwhelmingly produced [295]. For carboxylations in the presence of formate ester similar regiocontrol by simply changing the ligand was reported by Lin and Alper [296]. An electrochemical hydroesterification reaction using Pd salts as catalyst was used for the carbonylation of non-functionalized olefins. Although anodic regeneration of Pd(II) enables us to dispense with ligands and co-catalysts, the reaction lacks practical applications because of the very low turnover frequency (TOF) of 0.2–0.4 [297].

The effect of different iodide promoters on the hydrocarboxylation of olefins in the presence of Ru catalysts was studied exhaustively [298]. Remarkably, the use of ionic iodide as promotor increased the relative rate of the hydroesterification of ethylene by more than 1200 times. Ru-catalyzed hydroesterifications of mono-olefins with primary alcohols were also described. For instance, the reaction of propene and methanol at temperatures between

230–250°C and pressures above 150 bar produced butanoic acid in yields exceeding 65% [299]. Mechanistic studies confirm that the primary alcohol acts as CO/H₂ source.

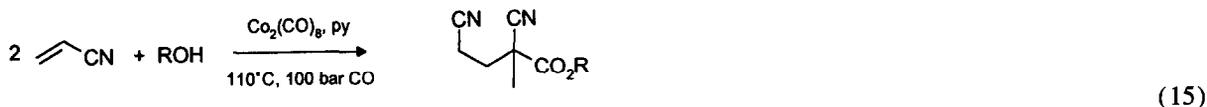
BASF has developed a three-stage process for the synthesis of adipic acid from butadiene containing C₄ cut [290] (g). The first stage [Eq. 13] uses a fairly high concentration of HCo(CO)₄ and pyridine as catalyst system to ensure rapid carbonylation of butadiene to give methyl pent-3-enoate, thus avoiding typical side reactions like dimerization and oligomerization. In the second step (Eq. 14), the concentration of pyridine as ligand must be low because it has an inhibitory effect on the hydroalkoxycarbonylation. In situ isomerization to the 4-pentenoic acid ester is a prerequisite for the subsequent carbonylation which yields dimethyl adipate. After hydrolysis of the ester, adipic acid is obtained with an overall selectivity of about 70% [290] (g). The commercial status of this process is unknown.



Depending on the reaction conditions, the carbonylation of dienes could lead to unsaturated and/or saturated mono and/or diacids or diesters, with dimerization and carbonylation reactions occurring in some cases. Examples include the formation of esters of 3,8-monodienoic acid by Pd-acetate-catalyzed carbonylation of butadiene in alcohol [300] and the oxidative carbonylation of butadiene in methanol catalyzed by PdCl₂ to give dimethyl-2-butene-1,4-dicarboxylate [301]. The Pd-catalyzed hydrocarboxylation of substituted 1,3-dienes yields unsaturated mono acids in the presence of phosphine ligands and formic acid [302].

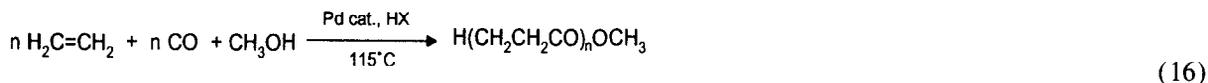
In combination with the incremental advances in reaction conditions, especially towards low-pressure carbonylations, this chemistry was increasingly used to synthesize advanced building blocks. In this respect hydrocarboxylation reactions of functionalized olefins have been used for the synthesis of fluorinated acids [303], silylated esters [304], and β-amino acids [305]. Important representatives of higher value acids are the commercially significant 2-arylpropionic acids. Despite research efforts which led to achievements [306] a catalyst system which fulfills technical needs has yet to be developed. Best optical yields so far were reported by Alper et al. who claims enantioselectivities of 84% with TON of 7–8 for the synthesis of ibuprofen with PdCl₂/CuCl₂ as catalysts and 1,1'-binaphthyl-2,2'-diyl hydrogen phosphate as the ligand in mixtures of HCl and tetrahydrofuran [307]. The same reaction conditions have been applied to the asymmetric cyclocarbonylation of but-2-en-1-ol to yield 1-methylbutyrolactone [308]. Best enantioselectivities up to 61% (49% yield) afforded poly-L-leucine as ligand.

Following the trend to prepare polyfunctional intermediates as building blocks via tandem reactions Markó et al. developed an efficient one pot hydroesterification–Michael addition [309] (Eq. 15). Thus, hydroalkoxycarbonylation of acrylonitrile with alcohols proceeds in the presence of catalytic amounts of Co₂(CO)₈ and pyridine bases to yield 2,4-dicyano-2-methylbutanoic acid esters. The yield of the desired products (up to 90%) strongly depends on the pyridine/cobalt ratio.



3.1.1.2. Oligomerizations and polymerizations with CO

Several Pd(II) catalyst systems have been reported, which effect perfectly the alternating copolymerization of olefins, particularly ethylene with CO to yield low-cost polyketones (Eq. 16) [310]. Apart from Pd, Rh catalysts have also been used for copolymerization [311].



The catalyst systems used for copolymerization have typically employed Pd(II) salts in alcoholic solvents in combination with acids, mono- or bidentate phosphines, or bidentate nitrogen ligands and frequently oxidants such as benzoquinone. Drent et al. developed a highly efficient homogeneous Pd catalyst system for terpolymerization of ethylene, propylene and CO. The essential features of the catalyst system are the equimolar combination of a 1,3-bis(diphenylphosphino)propane as ligand with a Pd(II) species in which the counter ions are weakly coordinating [312]. High rates with TON of more than one million per Pd center were obtained in methanol as solvent. The reaction is suggested to proceed via alternating sequence of CO and alkene insertion in Pd–C bonds [312]. An alternative mechanism involving Pd carbene intermediates was recently proposed [313]. It has been reported that the alternating copolymerization of CO and 4-*tert*-butylstyrene represents an example of living alternating copolymerization, which is very rare [314].

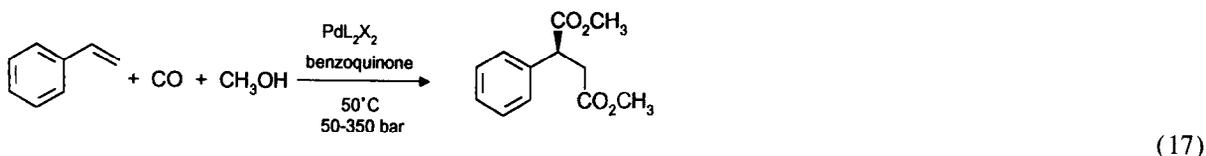
The inherent structural features (β -dicarbonyl unit) of olefin/CO copolymers suggested initial concern about long-term stability of these materials. Very recently Shell Chemicals found an economic solution to this problem. Polyketones on ethylene/CO basis with randomly incorporated propylene will be produced with a total capacity of 20,000 t/year as from 1996 [315].

3.1.1.3. Oxidative carbonylations

Palladium chemistry dominates this area and the main problems are related to the efficient reoxidation of Pd(0). For this purpose the use of nitrites has been studied for oxidative carbonylation of ethylene and propylene [316]. It appears that Pd(IV)NO⁻, which is in equilibrium with Pd(II)NO⁺, plays an important role in the course of the reaction.

Considerable interest has been paid by industry to the oxidative carbonylation of styrene as a promising method of producing cinnamic acid derivatives. The catalyst systems used ordinarily contain Pd and Cu salts as well as other metals as co-catalysts. A detailed study of the most active catalyst system consisting of PdCl₂, CuCl₂, Cu(OAc)₂ and, Mn(OAc)₂ showed that the introduction of Mn(OAc)₂ as additive substantially increased the activity [317].

Bisalkoxycarbonylation of olefins to succinate derivatives has been described with a number of catalysts, among them PdCl₂ and butyl nitrite [316], Pd(OAc)₂, O₂ and benzoquinone [318], as well as Pd(acac)₂ and di-*tert*-butylperoxide [319]. The first stereoselective version of this reaction was developed by Consiglio et al. [320] (Eq. 17). The bisalkoxycarbonylation of styrene using chiral PdL₂X₂ complexes and benzoquinone proceeds with enantioselectivities of up to 93% in the presence of chiral biphenylphosphines, albeit that the chemoselectivity of the reaction was lower.

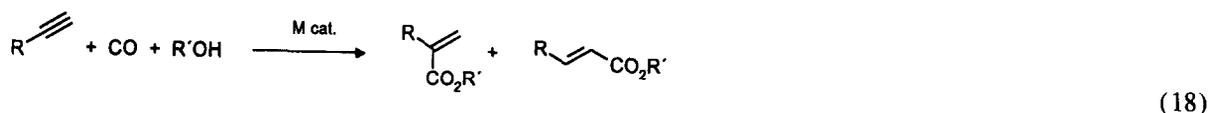


Processes that are reminiscent of succinate formation include intramolecular dialkoxycarbonylations [321], e.g. of 3-butenols [322], and 4-pentenols [323], as well as oxidative carbonylation of unsaturated ketones to give spiroacetals [324].

3.1.2. Carbonylation of alkynes

3.1.2.1. Hydrocarboxylations and related reactions

In principle, the same catalyst metals may be used for the carbonylation of alkynes as for the carbonylation of alkenes, but the reaction conditions are usually milder. The carbonylation of alkynes has been dominated industrially by the BASF process for acrylic acid (100,000 t/year) using NiBr_2/CuI as catalyst. Because of the feedstock change from acetylene to propylene the importance of this process is now diminishing. Most of the synthetic work in the area of alkyne carbonylation has been devoted to controlling regio- and stereoselectivity by using new catalyst systems, although practical applications will rely mainly on cheap starting materials, which will only be accessible in very rare cases. By using terminal alkynes instead of acetylene hydrocarboxylation reactions yield either 2- and/ or 3-substituted acrylic acid derivatives (Eq. 18).



The selective formation of 2-substituted acrylate esters using nickel cyanide under phase transfer conditions [325] or with Pd phosphine catalysts has been described [326]. Furthermore, hydroaminocarbonylation of terminal alkynes also proceeds regioselectively in the presence of Pd complexes and iodide promoters in diethylamine under considerably mild conditions [327]. This chemistry has been used for the synthesis of pharmacologically interesting amino acids [328]. In the past, catalysts based on Ni and hydrogen halides were considered to be far superior to all other catalysts for the carbonylation of alkynes [290] (g). Thus, it is remarkable that Drent et al. disclosed for the first time a highly efficient catalyst system based on Pd(II) species, 2-pyridyl diphenylphosphine, and an acid containing weakly coordinating anions. High TON of more than 40,000 mol/gAt. Pd·h and selectivities of up to 99.95%, especially for the carbonylation of propyne to methyl methacrylate were obtained [329]. Surprisingly, by simply changing the ligand from TPP to 2-pyridyl diphenylphosphine the catalyst activities were increased by more than three orders of magnitude.

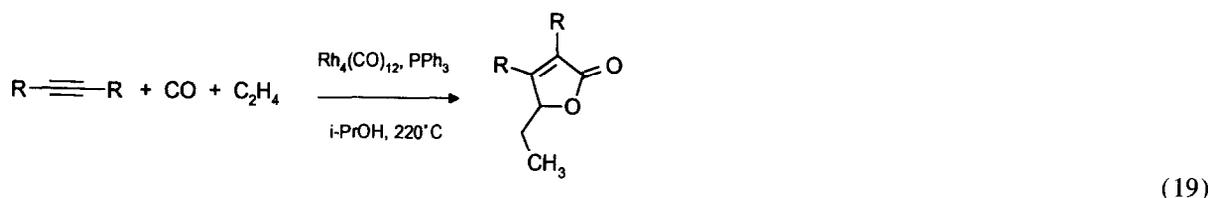
Treatment of alkynes with carbon monoxide in the presence of a bimetallic catalyst system consisting of CoCl_2 , KCN, and NiCN_2 directly yielded saturated carboxylic acids with good selectivity for the branched-chain isomer [330].

Biscarboxylations of alkynes to yield maleic and fumaric acid derivatives in the presence of Pd catalysts and of an oxidant have been reported [331]. Recently developed electrochemical reoxidation of palladium [332] or using PdI_2 with iodide promoters as catalyst [333] avoided the use of stoichiometric quantities of reoxidant, e.g. CuCl_2 .

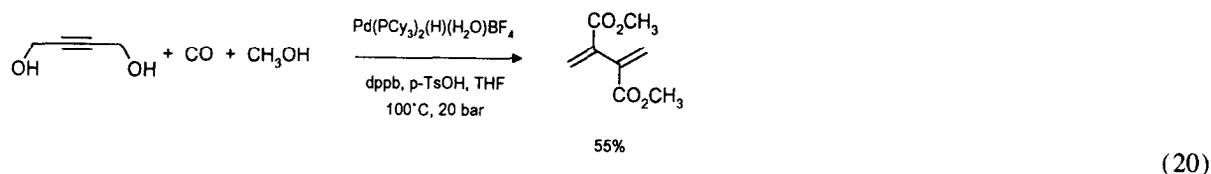
3.1.2.2. Others

In organic synthesis much of the work over the last 15 years has been devoted to the development of new tandem procedures, which effectively create a number of bonds in a consecutive manner. The various possibilities of cycloaddition reactions of alkynes and alkenes with CO have been reviewed [334]. Transition metal-catalyzed examples for this chemistry are the synthesis of cyclopentenones (*Pauson–Khand* reaction) [335], cyclopentadienones [336], and furanones [337]. Among these methods the cocyclization of alkynes with CO and alkenes by cobalt complexes leading to cyclopentenones has been used extensively on a stoichiometric basis. Despite the intensive research efforts and numerous synthetic applications [335] only two reports on catalytic *Pauson–Khand* reactions by Rautenstrauch et al. [338] and by Jeong et al. [339] have appeared so far.

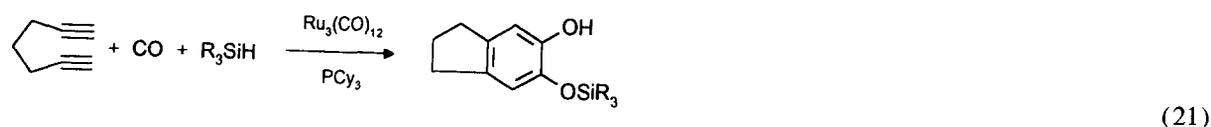
Rh-catalyzed synthesis of 2(5H)-furanones from alkynes under water–gas shift reaction conditions was studied [337]. Both internal and terminal alkynes could be applied as substrates. The furanone framework is combined by the reaction of the alkyne with one molecule of hydrogen and two molecules of CO. Related 5-ethyl-2(5H)-furanones were prepared by $\text{Rh}_4(\text{CO})_{12}$ -catalyzed carbonylation of an alkyne and ethylene in the presence of alcohols as hydrogen source (Eq. 19) [340].



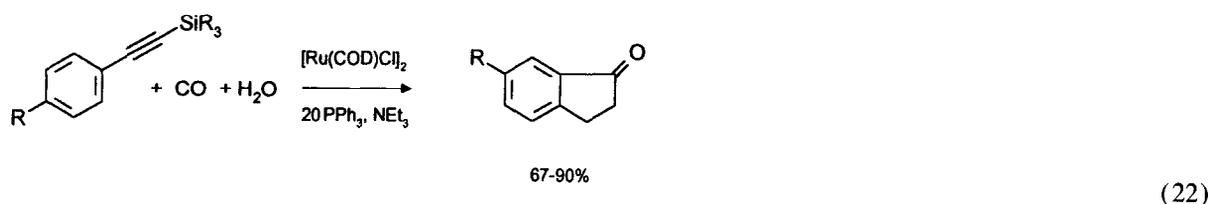
Interestingly, chemoselectivity switched to 1-penten-3-one when hydrogen is used only [341]. Furanones are also formed when propargylic alcohols were carbonylated with bis(dibenzylidene acetone)-Pd and 1,4-bis(diphenylphosphino)butane [342]. The reaction of CO with propargylic derivatives has been the subject of many investigations [343]. Depending on the catalyst (Ni, Pd) it is possible to synthesize either dienoic acids (Eq. 20), allenic acids, or unsaturated diacids [342].



Despite multiple functionalization possibilities none of these reactions is used commercially. An unusual example of carbonylation of 1,6-diyne was recently reported by Murai et al. [344]. 1,6-Heptadiyne reacts with carbon monoxide and *tert*-butyldimethylsilane in the presence of $\text{Ru}_3(\text{CO})_{12}$ and tricyclohexylphosphine to give a 5,6-dihydroxyindan derivative (Eq. 21). It is suggested that a ruthenium carbonyl complex rearranges during the catalytic cycle to form an oxacarbene complex.



Another example of potentially useful cyclocarbonylation leads to indenones, which are valuable intermediates, e.g. for metallocene ligands. Under water-gas shift reaction conditions aryltrimethylsilylacetylenes undergo rhodium-catalyzed desilylative carbonylation to give 2,3-dihydro-1H-inden-1-ones (Eq. 22) [345].



3.1.3. Carbonylation of CX compounds

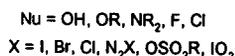
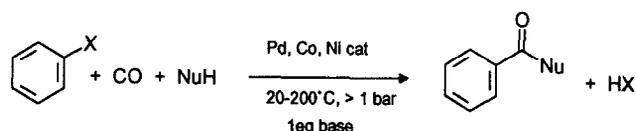
3.1.3.1. Reactions of aryl- and vinyl-X

From an industrial point of view organic halides are generally a less attractive feedstock for the synthesis of benzoic acid derivatives compared to toluenes which can lead to benzoic acids via air oxidation. Thus, their use is technically restricted to the synthesis of higher value fine chemicals and complex synthetic intermediates.

Based on the pioneering work of Heck and coworkers during the mid-seventies aryl- and vinyl-X carbonylations (*Heck carbonylation*) [346] have been used extensively in organic syntheses [347]. Much effort has been under-

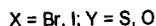
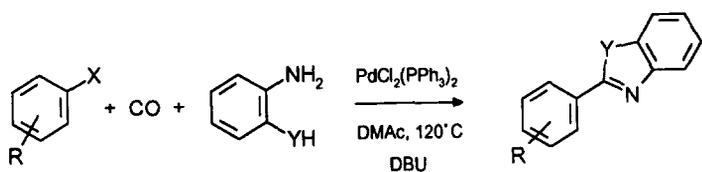
taken in the extension of this form of chemistry by the use of new starting materials and by combining the carbonylation step with new modes of trapping reactions of the intermediate acyl–metal complex. The combination of metal-catalyzed C–C coupling reactions with carbonylation chemistry to develop regio- and stereoselective atom economic cascade reactions has been a major subject of interest. This resulted in a number of new inter- and intramolecular methods for complex organic intermediates, mainly heterocycles. Despite its potential, none of the methods described so far has been used for commercial production. This is partly due to the low catalyst activities. TOF remain usually below 20 h^{-1} . To be of practical value, more research is clearly needed in future, which takes technical questions like catalyst activity (TON, TOF), catalyst lifetime, and recycling into consideration.

Most of the work reported during the last 15 years used corresponding aryl halides, especially bromides and iodides as starting materials and metal catalysts capable of oxidative addition to a C–X bond, such as Pd or Co and very seldom Ni complexes [348]. Moreover, diazonium compounds [349], triflates [350], alkyl- or arylsulfonates [351], fluorosulfonates [352], or iodoxyarenes [353] although technically not very important, were used as starting materials because of the ease of activation. Depending on the reaction media it is possible to synthesize either acids [354], esters [355,356] amides [357], and acid fluorides [358] (Eq. 23).



(23)

Moreover, aryloxazoles [359], arylthiazoles [360], anhydrides [361], and imides [362] are accessible via *Heck* type carbonylations (Eq. 24).



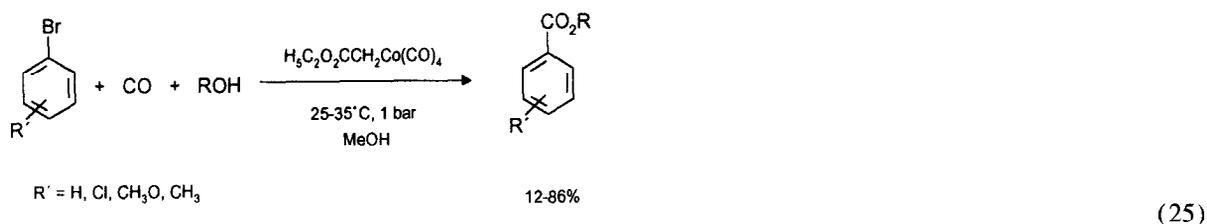
74–97%

(24)

In case of the carbonylation of iodo or bromo compounds it has been shown that the rate-determining step of the reaction is the nucleophilic attack on an acyl metal intermediate. Thus, amidation proceeds more rapidly than esterification under similar conditions. Stereospecificity in carbonylations of *cis* or *trans* vinylic halides is also higher for amidations (100% retention) compared to esterifications (90–95% retention).

The mechanism of the alkoxycarbonylation has been investigated in detail by cylindrical internal reflectance–Fourier transform infrared spectroscopy (CIR–FTIR). Infrared spectra of the active reaction at high alcohol concentration show that the dominant Pd complex does not contain a carbonyl group, consistent with a rate-limiting step involving oxidative addition. At low MeOH concentrations the Pd–acyl complex predominates and the rate strongly depends on the basicity of the base [363].

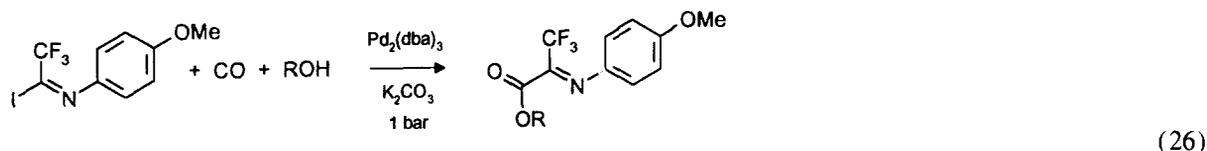
Because of the relatively high cost of Pd it is significant that cobalt–carbonyl complexes catalyze carbonylation of aryl and vinyl halides to acids at low CO pressure under conditions of photostimulation [364]. Photolysis to a coordinatively unsaturated 16-electron cobalt species seems to be the key reaction step. Foa et al. discovered a more practical solution because photochemical regeneration of the catalyst could be avoided if an alkylating agent, e.g. chloroacetate is added [365]. The resulting alkyl Co complex $\text{CH}_3\text{O}_2\text{CCH}_2\text{Co}(\text{CO})_4^-$ promotes carbonylation of aryl and vinyl halides under mild conditions (1 bar CO, 60°C) in good yields (Eq. 25).



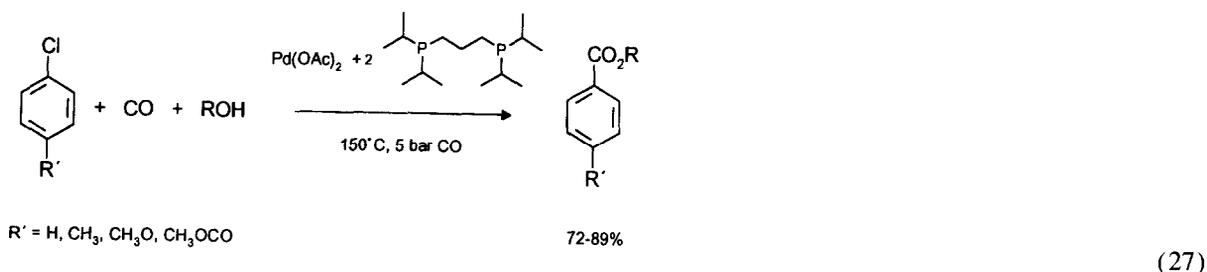
Carbonylation of aromatic halides with Pd catalysts and phase transfer systems, e.g. polyethylene glycol [366] or water-soluble catalysts [366] give satisfactory yields of benzoic acids. A study on the application of solid catalysts for carbonylation of aryl halides showed that Pd supported on charcoal was the most active system [367]. The carbonylation activity increased with the addition of a small amount of water to the reaction solvent methanol, but mixtures of benzoic acid and methyl benzoate were formed.

As regards alkoxy carbonylations, solid–liquid phase transfer conditions have been described to lead to improved yields of butylbenzoic acid ester [368] compared to the reaction conditions originally described by Heck et al. Beside natural product synthesis, Pd-catalyzed alkoxy carbonylations have been applied to syntheses of heat resistant aromatic polyesters and polyamides [369]. For the synthesis of model compounds for polyesters a study of the effect of added base for Pd-catalyzed aryloxy carbonylation has been performed [370]. Interestingly, conventional bases like Na acetate and tertiary amines lead only in low yield to the desired product, while cyclic amidines drastically increase the rate of reaction and the yield.

Besides the combination of an alcohol and base alcoholate complexes of various elements like B, Al [371], Sn [372] and Ti [355] can act as alkoxide sources in metal catalyzed alkoxy carbonylations. A promising approach to otherwise inaccessible fluorinated amino acids has been designed by Uneyama et al. [373] (Eq. 26). Palladium catalyzed carbonylation of an imido iodide in the presence of benzyl alcohol yielded the corresponding imino ester, with further transformation giving quaternary amino acids.



A breakthrough has been achieved in substitutive carbonylation of aryl chlorides, which is of industrial interest. Oxidative addition of an unsaturated metal complex to aryl chlorides is thought to be the rate limiting step in the reaction. Different strategies have been successfully pursued to overcome the lack of reactivity for oxidative addition. Milstein et al. [374] described very active palladium complexes based on the electron rich and bulky chelating diphosphine 1,3-bis(diisopropylphosphino)propane (Eq. 27).

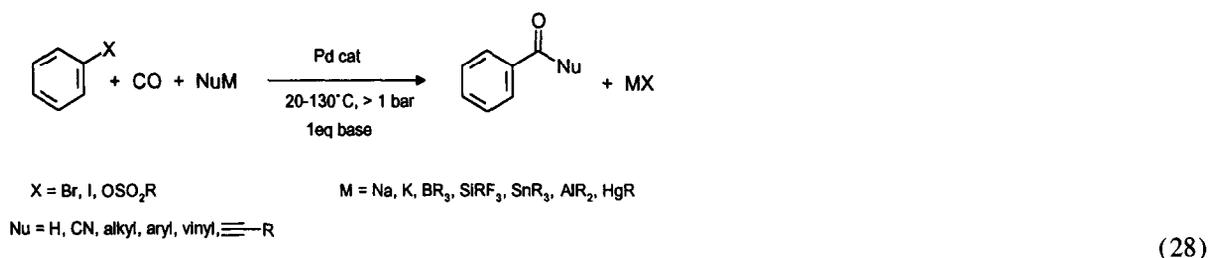


Likewise, Osborn et al. [375] and Alper and Grushin [376] suggested Pd complexes with phosphines which possess both high basicity ($\text{p}K_a > 6.5$) and defined steric hindrance. Best results for the carbonylation of chloro-

benzene under 30 bar of CO showed palladium complexes with triisopropylphosphine or tricyclohexylphosphine. Other methods of functionalizing chloro aromatics are photochemical activation [377], stoichiometric utilization of tricarbonyl(chloroarene)chromium complex [378] or using heterogeneous Pd catalysts under more drastic reaction conditions [379]. It is important to notice that certain N-heteroaromatic chlorides are much more readily carbonylated, due to the reduction of electron density in the aromatic ring and stronger polarization of the C–Cl bond [380].

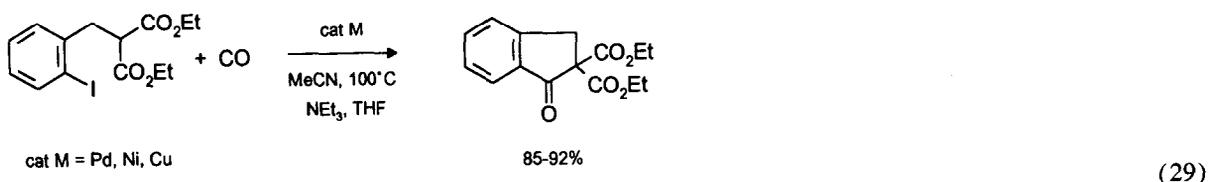
Depending on the catalyst system and the reaction conditions, especially at elevated CO pressures, it is possible to achieve double carbonylation reactions to 1-keto carboxylic acid derivatives [381]. Mechanistic investigations have recently shown that double CO insertion into the Pd–carbon bond does not occur directly, instead the terminal step of double carbonylation is generally a coupling reaction between metal-bonded acyl or alkoxycarbonyl or amidocarbonyl groups and CO [382].

Besides typical benzoic and vinylic acid derivatives aldehydes [376,383], ketones [384], aryl cyanides [385], aryl acetylenes [386], and their derivatives [387] are accessible via nucleophilic attack of the intermediate acyl metal complex by the corresponding hydrogen or carbon nucleophiles (Eq. 28).



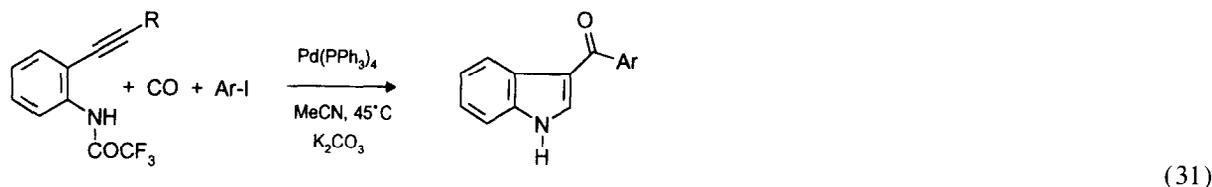
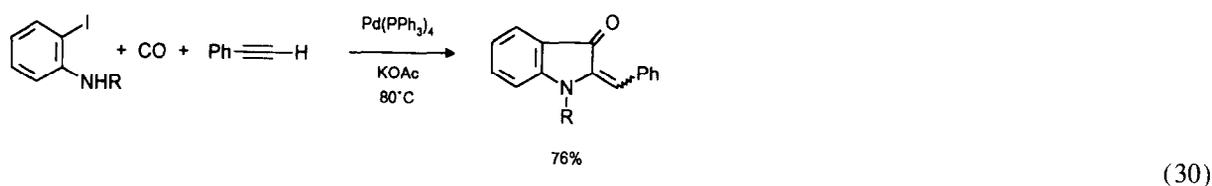
Even anionic metal complexes like $[\text{Co}(\text{CO})_4]^-$ can act as nucleophile and lead to arylcobalt complexes as products [388].

Instead of intermolecular reactions of the acyl palladium complex a number of intramolecular trapping reactions have been developed and used in organic synthesis in recent years. Some typical examples [389] include the carbonylation of 2-halophenols or 2-haloanilines to O- or N-heterocycles, intramolecular enolate or enamine trapping to isocoumarins or quinolinones. For carbonylative cyclization to indanones and tetralones a study on the feasibility of different late transition-metal complexes has appeared. Apart from palladium, copper and nickel derivatives are also able to catalyze the reaction (Eq. 29) [390].



The combination of double carbonylation with intramolecular trapping reactions has been used for the synthesis of isatin from 2-iodoaniline [391], ketolactone from 2-bromophenylbutadiene [392] and other heterocycles [393].

Related tandem reactions with three components (aromatics, alkynes and CO) were used for the synthesis of derivatives of flavone [394], aurone [395], indoxyl [396], as well as furanones [397]. The broad variety of synthetic possibilities of this chemistry even by minor changes of the reactants is nicely demonstrated by the reaction of 2-haloanilines with CO and alkynes. In case of a one pot reaction indoxyl derivatives are produced (Eq. 30) [396]. The reaction is initiated by oxidative addition of a palladium(0) complex to the aryl halide. Interestingly, the resulting arylpalladium(II) complex reacts chemoselectively with CO and not with the alkyne. As shown in Eq. 31 and contrary to the last example, the consecutive reaction with an alkyne as the first step and CO and another aryl halide as the second step leads to 3-acylindoles [398].



It deserves mention that related palladium-catalyzed C–C coupling cascades have been combined with a carbonylation terminating step [399]. In such cases vinyl- or alkyl-palladium(II) intermediates generated in situ were trapped by carbonylation reactions, mainly carboxylations.

Not only aryl- and vinyl-X compounds with X as an electron withdrawing group can be carbonylated, organo-elemental derivatives can also serve as starting materials [400]. The technical importance of this type of reaction seems to be low.

3.1.3.2. Reactions of alkyl-X

The carbonylation of alcohols to give carboxylic acids is one of the most important applications of carbonylation chemistry. Especially the direct synthesis of acetic acid from methanol and carbon monoxide is of major commercial significance. Today the Monsanto process using rhodium catalysts is the dominant technology in this field having superseded the classical BASF process. The kinetics of the Rh-catalyzed carbonylation of methanol have been investigated in detail. On a molecular level, this process is well understood [401] to involve the rate-determining nucleophilic attack on alkyl iodide by the anion $\text{RhI}_2(\text{CO})_2^-$ (Eqs. 32–36).



There has been considerable industrial interest in the extension of this reaction, using the same type of catalyst, to the production of acetic anhydride by carbonylation of either dimethyl ether or methyl acetate [402]. Thus, Eastman Chem. Co. have succeeded in the development of a new process for acetic anhydride based on the carbonylation of methyl acetate (Eq. 37) [403]. Since 1983 approximately 240,000 tons of acetic anhydride per year have been produced via this route [404].

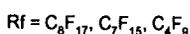
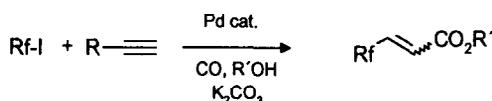


A similar process for the production of acetic acid and acetic anhydride in any desired ratio has been developed by Hoechst AG [402]. Mechanistic studies [405] show that the active catalyst appears to be *cis*- $\text{Rh}(\text{CO})_2\text{I}_2^-$. High-pressure infrared cell measurements suggest that molecular hydrogen (2–7%) converts *trans*- $\text{Rh}(\text{CO})_2\text{I}_2^-$ into the active intermediate [406].

The rates of the rhodium-catalyzed carbonylation of primary alcohols have been measured [407]. It has been shown in more detail that the rate decreased in the order $\text{MeOH} > \text{EtOH} > \text{n-PrOH}$ with relative rates of 21:1:0.47 at 170°C. In all cases, the reaction rate is of first order in both Rh and added HI and independent of CO pressure.

In general, palladium complexes are much less active than Rh-based catalysts. In the past it was also claimed that they are not suitable as catalysts for carbonylation of higher alkyl derivatives owing to the strong tendency of alkyl-palladium complexes to undergo β -hydride elimination. Interestingly it was reported that tetraalkylureas as solvents prevent elimination side reactions for Co- and Pd-catalyzed carbonylation of various organic halides [408]. Dibromomethane has been carbonylated with Co, Pd and Rh to dimethyl malonate at 100°C and 30 bar of CO [409].

An interesting development in the area of perfluorinated olefins has been described (Eq. 38). Perfluoroalkyl iodides react with terminal olefins or acetylenes and stoichiometric amounts of base in alcohols under CO pressure with $\text{PdCl}_2(\text{TPP})_2$ as catalyst to give β -perfluoroalkyl-substituted alkanates or alkenates selectively [410].

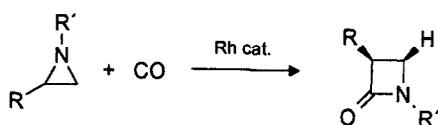


40-67%

(38)

Besides alkyl halides, alkyl sulfonates also react with CO and alcohol in the presence of catalytic amounts of Co catalysts to yield the corresponding esters. Addition of sodium iodide increased the yields from 32 to 72% [411].

As a special type of carbonylation, the ring expansions of strained hetero rings like aziridines [412], azetidines [413], epoxides [414], and thiiranes [415] deserve mention. In industry considerable efforts were directed to the carbonylation of ethylene oxide to β -hydroxypropionic acid derivatives [416]. In the case of aziridines, the focus has been on enantioselective reactions to β -lactams (Eq. 39) [417].



(39)

3.1.3.3. Reactions of benzyl- and allyl-X

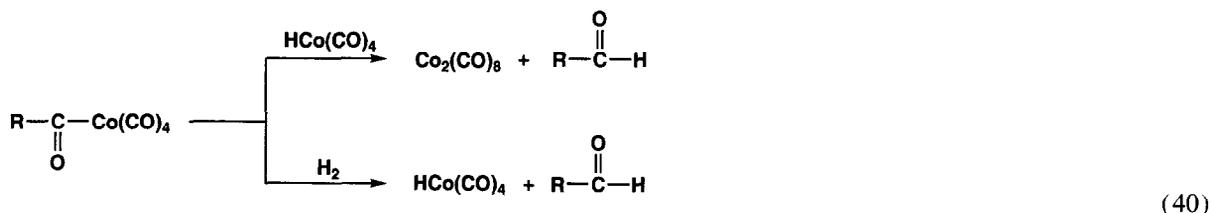
The transition metal-catalyzed carbonylation of allylic and benzylic derivatives offers a valuable tool for the synthesis of 3,4-unsaturated carboxylic acid derivatives and aryl acetic acid derivatives, respectively. Catalysts used for this type of transformation are Ni [418], Co [419], Rh [420], Pt [421], Fe [422], but mainly Pd catalysts [423] for activity and selectivity reasons.

Unlike aryl halides, benzylic and allylic derivatives are susceptible to nucleophilic attack and elimination reactions. Thus, over the past 15 years of carbonylation of allylic compounds, considerable effort has been directed to the development of milder and more selective reaction conditions, e.g. atmospheric pressure carbonylations [424] and expanding synthetic methods, e.g. via tandem reactions. In the case of catalytic carbonylation of allylic and benzylic halides two-phase systems with phase transfer conditions [425] have been introduced and extensively used. Usually the reactions were performed with an excess of base in a biphasic system with a metal catalyst in the organic phase. Surfactants are used as phase transfer catalysts. They appear to have an important transport function in moving the cobalt carbonyl salt from the aqueous phase to the organic droplets.

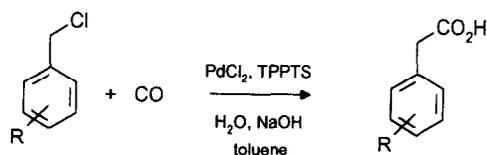
Interestingly, Alper and Amer showed that certain lanthanide salts can effectively promote nickel cyanide catalyzed carbonylations. The Lewis acid character of the lanthanide compound probably accelerates the carbonyl insertion process of the benzyl metal complex [418] (a). This type of co-catalysis should be applicable to other types of Lewis acids, too. While studying the structure of the phase transfer co-catalyst it was observed that

benzyltrialkylammonium salts were easily carbonylated. In some cases the yields of arylacetic acids are higher compared to the carbonylation of the corresponding benzyl halides [426].

It has been reported that the carbonylation of benzyl chloride to phenylacetic acid is used industrially by Montedison (Eq. 40, [20]). The carbonylation is conducted in a two-phase medium of a non-polar solvent and 40% aqueous NaOH solution with a cobalt carbonyl complex and a benzyltrialkylammonium surfactant [427].



A major drawback for most carbonylations of benzylic and allylic halides is the large amount of catalyst (1–20 mol-%) and phase transfer reagent (5–10 mol-%) needed for high conversion and yields. In order to expand industrial use, improvements have to be made in the future. Recently, a new approach [156,428] using water-soluble Pd catalysts with TPPTS as ligand offer efficient product separation along with more active catalyst systems reaching TON of more than 1500 (Eq. 41) [156].



TPPTS = sodium trisulfonatophenylphosphine

(41)

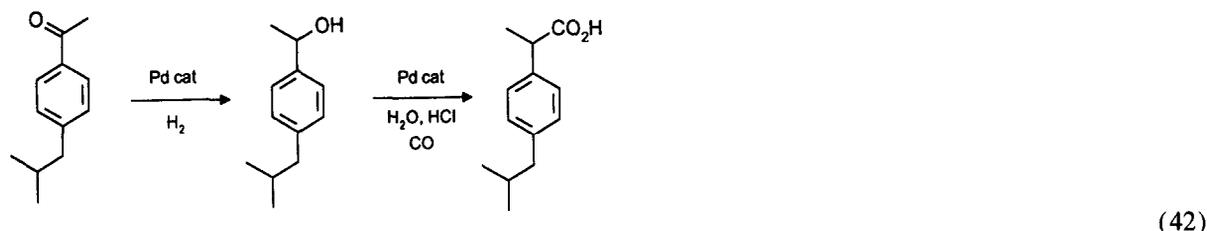
An alternative concept providing easy product separation is claimed to support $[\text{Co}(\text{CO})_4]^-$ on an anion-exchange resin [355]. But only a total TON of about 145 was obtained and no long-term study on the leaching of the metal was done, which usually takes place in case of heterogenized systems.

The synthesis of phenylacetic acid esters is not possible by common phase transfer procedures, but could be realized by direct carbonylation with Pd or Rh catalysts in the presence of Ti, Zr or Al alkoxides [371], borate esters [429], ethers [430], or formates [431]. In addition, supported base on basic alumina in the presence of cobalt carbonyl complexes leads to moderate yields [432]. Fuchikami et al. [433] reported the carbonylation of benzyl bromide catalyzed by Pd complexes under base free conditions in the presence of different types of molecular sieves (85% yield in THF).

Owing to the absence of salt by-products, the carbonylation of allylic and benzylic alcohol derivatives such as acetates [434], carbonates [435], ethers [436], phosphates [434] (a) [437] and alcohols [438] is more important today. According to Murahashi et al. [434] (b) the reactivity of the leaving group of allylic substrates decreases in the order $\text{Br} > \text{OP}(\text{O})(\text{OEt})_2 > \text{Cl} > \text{OCOCF}_3 > \text{OCO}_2\text{Et} > \text{OCOPh} > \text{OCOMe}$. No reactivity was found for OPh, NEt_2 and OH. For allylic acetates, carbonylation has been a problem for some time. It has been shown that for the intermediate allylpalladium acetate complex the back reaction to form allyl acetates proceeds faster than the insertion of CO into the complex [439]. Introduction of bromide ions as co-catalyst leads to a fast ligand exchange of the acetate with bromide. Therefore the resulting bromide complexes could be carbonylated in moderate to good yields (57–90%) [434] (b). A similar co-catalysis of chloride ions was observed in the carbonylation of 4-hydroxybenzyl alcohol to 4-hydroxyphenylacetic acid with palladium–hydrogen chloride systems [438] (c).

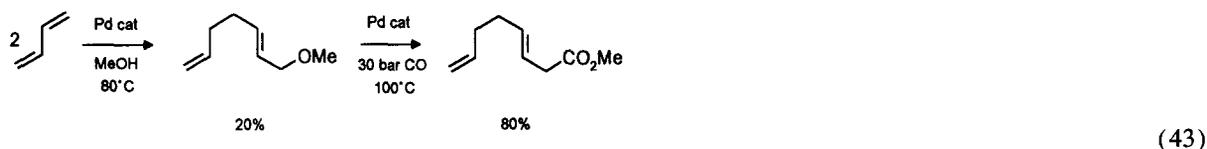
Special interest has been paid to the synthesis of profenes [440] like ibuprofen, naproxen, ketoprofen and others from 1-arylethanol derivatives (cf. Section 2.1.3.3.2.3.). Catalysts used for this transformation are Pd phosphine

complexes in concentrated HCl, to a lesser extent Ni phosphine complexes in the presence of alkyl iodides or Rh salts. Based on the Pd catalyzed carbonylation of 1-(4-isobutylphenyl)ethanol, which is produced via salt-free acylation of isobutylbenzene to 4-isobutylacetophenone and subsequent hydrogenation, the Hoechst Celanese Corporation [441] developed an ecologically superior process (Eq. 42) to produce ibuprofen. Production commenced in 1992 and totals 3,500 t/year [404].



Very limited work on profene synthesis via carbonylation has been reported from university groups. One exception is the stereoselective carbonylation of racemic benzylic bromides. The asymmetric reaction towards enantiomerically pure profenes could proceed a priori either by a kinetic resolution or by true asymmetric induction via the intermediacy of a trigonal substrate. Results obtained by Arzoumanian et al. [442] strongly suggest that the carbonylation of 1-methylbenzyl bromide with oxazaphospholene–Pd complexes is a kinetic resolution process with a discriminatively slow oxidative addition step. Best ee is about 64% at 9% chemical yield. Another possibility of synthesizing enantiomerically pure profenes is to start from optically pure benzyl derivatives. Baird et al. investigated the carboxylation of optically active benzyl carbonates with Pd catalysts. Enantiomeric excess was only modest [443]. Thus, the development of an efficient catalytic asymmetric carbonylation is still an existing challenge.

Pelargonic (*n*-nonanoic) acid, an industrially interesting synthetic fatty acid, has been prepared by butadiene telomerisation in the presence of methanol and subsequent carbonylation of allylic ethers and hydrogenation (Eq. 43) [436].



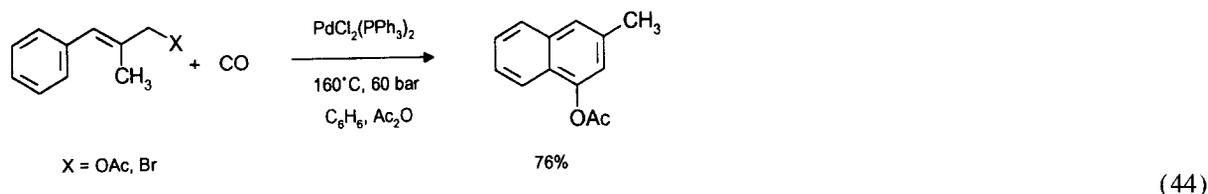
Comparative studies with respect to the catalysts showed that [(methyl-2-allyl)PdCl]₂ was superior to conventional Pd catalysts in the carbonylation step. Selectivities and catalyst activities still have to be improved to make the overall process commercially viable. Besides the carbonylation of benzylic and allylic alcohol derivatives, the reaction of benzylic thiols with CO in the presence of dicobalt octacarbonyl to yield phenylacetic acid esters has also been described [444].

So far catalytic carbonylations in the presence of oxygen nucleophiles to give unsaturated acids and their esters have been dealt with. Azacarbonylations to form amides from allylic derivatives are limited to high-pressure carbonylations of allylamines [445] and to decarboxylation–carbonylation of diethylcarbamic acid allylic esters [446]. Moreover, the carbonylation of allyl phosphates proceeds very efficiently under mild conditions to give the corresponding unsaturated amides in up to 86% yield in the presence of Rh carbonyl clusters e.g. Rh₆(CO)₁₆ as catalyst and phase-transfer co-catalyst. In contrast, Pd catalysts cause mostly allyl amines [437].

Carbonylation of benzylic chloride or allyl chloride with syngas in the presence of cobalt or palladium catalysts forming phenylacetaldehyde in 78% yield and 3,4-unsaturated aldehydes, respectively have been described [447]. Tandem CC coupling reactions of benzylic and allylic halides with CO and organoaluminum [448], organotin [449] or organoborane [450] compounds to ketones have been reported. This reaction has also been used as a key step in natural product synthesis for maolide [451]. For the reaction of 1-alkylbenzyl bromide with tetramethyl tin and CO interestingly PdCl₂(AsPh₃)₂ was a better catalyst than PdCl₂(TPP)₂ [452]. Related three component

coupling reactions of allyl benzoates, CO and zincioesters to prepare unsymmetrically substituted ketones were described by Tamuru et al. [453].

Allylic halogenides containing an additional functional groups in a suitable position, e.g. an alkene moiety or an hydroxy group produce the corresponding cyclopentenone derivatives or lactones, respectively via Pd catalyzed carbonylation [454]. Related cyclocarbonylation of cinnamyl halides or acetates to form polycyclic aromatics such as naphthol derivatives have been reported (Eq. 44). Moreover, the synthetic utility of the method was demonstrated by the synthesis of acetoxybenzofurans, acetoxyindoles, and acetoxycarbazoles [455].



Another type of elegant tandem reaction is the metallo-ene cyclization–carbonylation sequence which has been investigated in detail by Oppolzer et al. [456]. In the presence of Ni or Pd phosphine complexes intramolecular alkene allylation coupled with methoxycarbonylation provide various carbo- and heterocycles in one step. Interestingly these reactions are stereoselective. The ring junction is *cis* with nickel, while a similar reaction with palladium catalyst gives a *trans* product. The utility of Ni complexes for intramolecular metallo-ene reactions depends strongly on the metal ligand. For example in the case of the 2,7-octadienyl iodide carbonylation with dppb as ligand is faster than β -elimination [457].

Besides alkene allylation, the process of alkyne allylation coupled with carbonylation has also been developed [458]. Double functionalization of allyl chloride to 3,4-dichlorobutanoyl chloride in moderate yield has been reported by Tkatenchenko et al. [459]. This chlorocarbonylation is catalyzed by Pd salts in the presence of anhydrous HCl.

So far, only examples of carbon monoxide insertion in allylic precursors have been mentioned. Beside this typical reaction path addition processes are known, e.g. allylic amines react with CO in the presence of Rh catalysts to give butyrolactams [460]. Similar reactions of allylic alcohols to lactones using PdCl₂ under acidic conditions and in the presence of oxygen and cupric chloride [461] or with Pd phosphine catalysts under neutral conditions have been described [462]. Further processes are discussed in Section 3.1.1.

3.1.4. Carbonylation of aldehydes

The carbonylation of aldehydes has met with interest in the synthesis of glyoxylic acid and more importantly as an alternative ethylene glycol process. In the early eighties, hydrocarbonylation of formaldehyde to glycolaldehyde followed by hydrogenation was viewed as a potentially more viable route than the direct synthesis of glycol from carbon monoxide and hydrogen because of the severe and harsh reaction conditions for the latter process. But the decrease in oil prices in the mid-eighties made ethylene glycol synthesis from ethylene via ethylene oxide much more economical [463]. Hydrocarbonylation of formaldehyde [464] to glycolaldehyde has been carried out in the homogeneous phase using Co, Ru or most successfully Rh catalysts (Eq. 45).



Best results are obtained in amidic solvents with Rh catalysts and acid promoters. Up to 300 mol formaldehyde are converted per mol Rh per hour. The catalyst consists of Rh(acac)(CO)₂ with aromatic phosphines such as tris(4-chlorophenyl)phosphine as ligands.

Basic phosphine ligands tend to give rise to methanol. Thus, it has been concluded that a cationic Rh hydride is the key intermediate of the reaction. If it is sufficiently acidic, it will activate formaldehyde by protonation to form an Rh–CH₂–OH species, whereas if it is too hydridic, it will give rise to Rh–OCH₃ and to methanol as observed for

basic phosphines [465]. Besides hydrocarbonylation, direct carboxylation to glyoxylic acid is of commercial interest, but has not been investigated much. Acid catalyzed carbonylations, e.g. with H_2SO_4 , zeolites or sulfonated resins were described [466] under severe reaction conditions. Other aldehydes besides formaldehyde are much more difficult to carbonylate. An exception is the recently published carbonylation of electron-rich aromatic aldehydes to phenylacetic acid derivatives by palladium–phosphine systems in the presence of HCl [467].

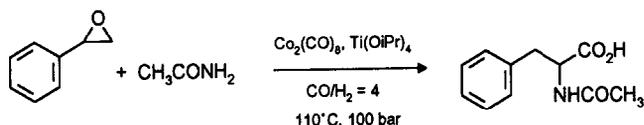
3.1.5. Amidocarbonylation

A remarkable and special case of the carbonylation of aldehydes is the amidocarbonylation [468] reaction originally discovered by Wakamatsu et al. [469]. In the presence of amides and catalytic amounts of Co complexes, aldehydes can be carbonylated directly to N-acyl amino acids. Although amidocarbonylation procedures cannot compete commercially against cheap natural sources or fermentation, for non-natural amino acids this salt-free process must be considered a viable alternative to the conventional *Strecker* reaction. Because of the interest in N-acyl amino acids as chelating agents, detergents and products for enhanced oil recovery this method has high potential for future industrial realization.

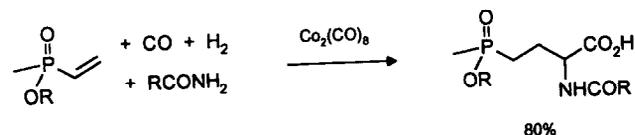
The effect of ligands on the synthesis of N-acetyl glycine and on catalyst recovery after the reaction was studied [470]. The best yield (78%) was observed with succinonitrile as ligand. Moreover, catalyst recovery increased from 50% to 85% on the basis of cobalt used. Besides using linear amides as starting materials, amido-carbonylation of butyrolactam, and caprolactam to prepare the corresponding amino acids has been demonstrated [470].

Applications of amidocarbonylation to the synthesis of heterocyclic compounds were developed [471]. A mechanistic proposal for amidocarbonylation has been published [472]. It is assumed that an N-acylenamine is the most active species for the reaction with $\text{HCo}(\text{CO})_4$ as catalyst. While butanal reacts with acetamide and syngas in the presence of $\text{Co}_2(\text{CO})_8$ in 72% to N-acetylnorvaline, secondary amides gave only poor yields [472]. By contrast, recent optimization studies of the amidocarbonylation reaction for sarcosinate synthesis have shown that the reaction of secondary amides could be performed under very mild conditions (50°C and 10–20 bar CO) with extremely high conversion (>99%) and selectivity (>95%) [473].

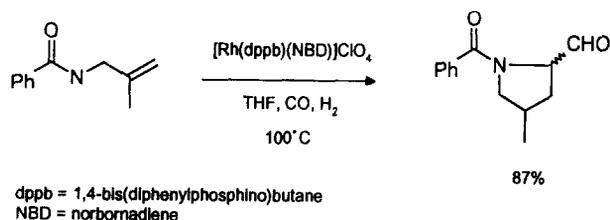
By combining known catalytic transformations to aldehydes with the amidocarbonylation reaction, new domino reaction sequences were developed. Whereas the amidocarbonylation of aldehydes is catalyzed only by Co carbonyl complexes for tandem reactions homogeneous bimetallic catalysts have been used more successfully [474]. In this respect, Ojima et al. reported the synthesis of phenylalanine, the key intermediate for Aspartame sweetener, directly from styrene oxide with Co carbonyl complexes and Ti isopropoxide (Eq. 46) [475]. The mild Lewis acid promotes the in situ rearrangement of the oxirane to the aldehyde.



The addition of an isomerization catalyst such as $\text{RhH}(\text{CO})(\text{TPP})_3$ allows the direct amidocarbonylation of allyl alcohols [476]. Another important synthetic development is the olefin hydroformylation–amidocarbonylation sequence [477], which was used for a variety of simple unfunctionalized olefins as well as certain diolefins. Alkenes containing various functionalities lead to a number of commercially valuable amino acid derivatives. Examples include the amidocarbonylation of ethyl acrylate to N-acetylglutamic acid ester [470], a precursor of monosodium glutamate and of vinyl phosphonate to a herbicide precursor (Eq. 47) [478].



Recently, a new type of amidocarbonylation reaction was discovered by Ojima et al. [479]. They described the first example of Rh catalyzed sequential double carbonylation of allylamides to 2-formylpyrrolidone derivatives (Eq. 48). By careful catalyst design it was possible to get the desired product in 87% yield with selectivities of > 99%.



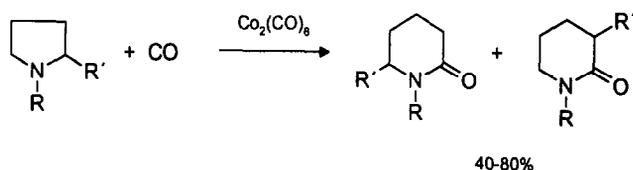
3.1.6. Carbonylation of nitrogen derivatives

The search for environmentally benign processes to replace phosgene has focused attention on homogeneous catalytic carbonylation [480]. Particularly the synthesis of carbamates and isocyanates either by reduction of aromatic nitro compounds or less often by oxidative carbonylation of amines has been studied. Isocyanates, which are important industrial intermediates in the synthesis of polyurethanes and pesticides, were synthesized from nitro aromatics typically in the presence of Pd [481], Rh [482], and Ru catalysts [483]. Despite promising results for model reactions, so far the reductive carbonylation of nitro aromatics has not been realized commercially due to insufficient selectivities, e.g. for TDI and high catalyst costs [484]. When conducted in alcohols, the reaction proceeds with improved rates and better selectivities to urethanes. Recently, modifications of catalyst and co-catalyst systems and the role of reaction conditions have been studied for this reaction [483]. The tolerance of various functional groups for nitro reduction with CO has been examined [485]. An impressive example is the chemo-selective reduction of *m*-nitrostyrene to *m*-aminostyrene in 91% yield in the presence of a catalyst system of $\text{Rh}_6(\text{CO})_{16}$ and tetramethyl-1,3-propanediamine.

Pd salts or complexes in the presence of acids and/or co-catalysts have been used in the oxidative carbonylation of amines for the synthesis of N,N' -disubstituted ureas and carbamates [486]. Asahi Chemical Industry has developed a catalyst system based on palladium black and iodide as an promoter [487]. At 160–170°C and 90 bar pressure (7% O_2) aniline is converted to ethyl phenylcarbamate with 96% selectivity. A study on the reactivity of palladium(II) methoxycarbonyl complexes in stoichiometric reactions with amines in the presence of acids and Cu co-catalysts showed that the Pd compound does not react directly with amines under mild condition [488]. For reoxidation of the carbonylation catalyst, oxygen in the presence of Cu salts, organic peroxides or electrochemical reoxidation were described [489].

Somewhat sophisticated catalysts like Co porphyrins [490] or Co(II) salen complexes [491] also afforded the N -carbonylation of amines with mixtures of CO and O_2 , albeit with very low TON. The related $\text{K}[\text{Ru}(\text{saloph})\text{Cl}_2]$ or $\text{K}[\text{Ru}(\text{EDTA-H})(\text{CO})]^-$ complexes (saloph = bis(salicylaldehyde)-*o*-phenylenediimine; EDTA = N,N -ethylenediamine tetraacetate) catalyze the oxidative carbonylation of primary and secondary amines as well as NH_3 in aqueous media (5–80 bar; 50–100°C) primarily to urethanes [492]. For example the reaction of cyclohexylamine in ethanol to cyclohexylurethane proceeds with a TON of 30 per hour [493].

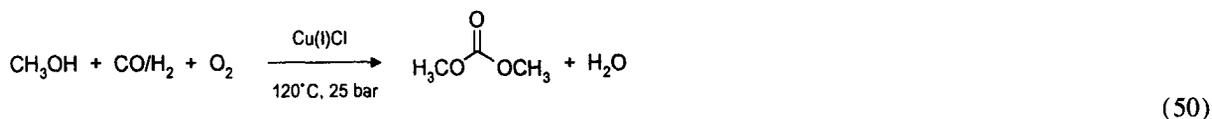
Unusual carbonylations have been described for the synthesis of carbamoyl chlorides starting from N -chloroamines [494], arylsulfonyl isocyanates from arylsulfonyl halides [495], and piperidones from pyrrolidines (Eq. 49) [496].



3.1.7. Other carbonylations

Examples of new processes in the area of oxidative carbonylations are syntheses of dimethyl carbonate, and dialkyl oxalates. Dimethyl carbonate is a safe and environmentally friendly substitute for highly toxic phosgene. Production based on the oxidative carbonylation of methanol was begun by Enichem in 1984 [497] on a 5,500-ton scale. In 1988 production was expanded to 8,800 tons per year [498].

For production of dimethyl carbonate a slurry of CuCl in methanol is treated with a mixture of syngas and oxygen (Eq. 50). At moderate methanol conversions (30–35%), the dimethyl carbonate yield is 100% based on methanol and 90–95% based on CO [499]. Another process for dimethyl carbonate via carbonylation of ethylene oxide and subsequent transesterification with methanol was developed by Bayer [500]. Reports indicate that this process was commercialized in 1984 [498].



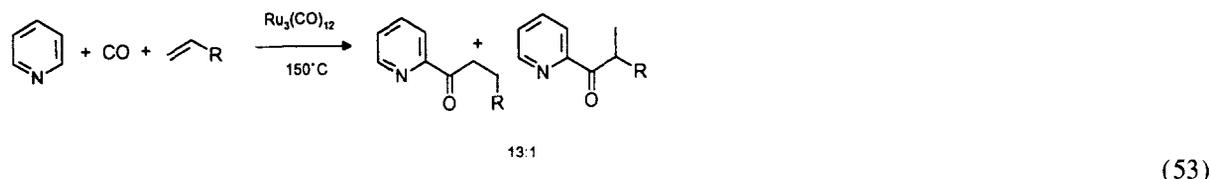
Oxidative carbonylation is of considerable commercial interest in the synthesis of dialkyl oxalates from alcohols and CO. The reaction occurs in the presence of Pd catalysts, along with suitable promoters. In the catalytic cycle, Pd can be reoxidized with the assistance of copper halides. An indirect process for oxalic acid based on this reaction has been commercialized by Ube Industries Ltd. on a scale of about 6,000 t/year. The process involves the reaction of alkyl nitrite and CO to dialkyl oxalate, which is hydrolyzed to oxalic acid. Alkyl nitrite is produced from the alcohol and nitrous oxide in the presence of oxygen. A heterogeneous gaseous phase process [501] as well as a liquid phase process (Eqs. 51, 52) [502] have been described for the oxidative carbonylation. In the liquid phase reaction n-butyl nitrite reacts with Pd⁰ on active carbon at 90°C and 60 bar CO. Selectivity to di-n-butyl oxalate is 94.6%. A by-product is di-n-butyl carbonate.



Because of the excellent selectivity, this process has been studied jointly by Ube Industries and Union Carbide for the synthesis of ethylene glycol. The feasibility of this process was demonstrated by Union Carbide in an integrated pilot plant [503]. With respect to the mild conditions and the excellent overall yield the process is the most attractive alternative to the current ethylene oxide route and is clearly preferred over direct CO hydrogenation.

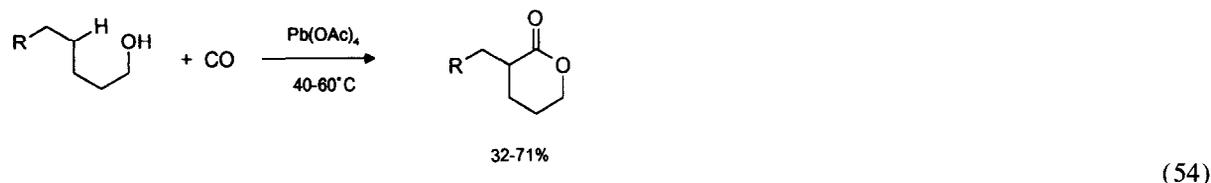
The introduction of CO into unactivated hydrocarbons by means of transition metal-mediated processes has been investigated quite intensively [504]. In this context studies on photochemical C–H activation have appeared [505]. For example phenylacetaldehyde can be synthesized photochemically from toluene and CO in the presence of Rh complexes [506]. Nevertheless, most procedures described are still far from being industrially viable because of inefficient catalysts. An exception is the catalytic regioselective acylation of pyridine with CO and olefins [507] in the presence of rhodium carbonyl cluster (Eq. 53). It is believed that the cluster framework remains intact during

the course of the acylation reaction. TOF of 160/h and 65% yield have been observed for the reaction with 1-hexene.



To improve catalyst efficiency for simple alkane activation the effect of metal additives on the reaction of cyclohexane with CO in the presence of a palladium(II) acetate–potassium persulfate–trifluoroacetic acid system has been investigated. Best results (TON 20 based on Pd; yield 4.3% based on cyclohexane) were obtained with Cu(II) acetate as co-catalyst [508].

A new lactone synthesis starting from saturated alcohols via remote radical carbonylation was realized recently (Eq. 54) [509]. In the presence of stoichiometric amounts of lead tetraacetate an oxygen-centered radical was generated from primary or secondary alcohols. After 1,5-hydrogen transfer reaction the carbon centered radical is trapped by CO. Finally oxidation and cyclization yield the lactones.



Other radical carbonylations [510] e.g. towards macrolides, cyclopentanones, and functionalized cyclopentanes were reported.

3.2. Technical developments

The last 15 years have shown that homogeneous catalysis is a promising tool for the refinement of chemicals. Synthetic methods which have reached successful application include the production of acetic anhydride (Eastman Chem., 240,000 t/year, 1983), polymerization of ethylene and CO (Shell AG, 20,000 t/year, starting in mid-1996), carbonylation of butadiene (BASF, pilot plant), synthesis of phenyl acetic acid (Montedison), synthesis of ibuprofen (Hoechst Celanese Corp., 3,500 t/year, 1992), and oxidative carbonylation to give dimethyl carbonate (Enichem, 8,800 t/year, 1988), and oxalic acid (Ube Industries, 6,000 t/year).

Apart from the transition metal-catalyzed methods already mentioned, other new industrial processes involving CO chemistry have been developed. Some examples of salt-free aromatic acylation chemistry using HF, BF₃ as reaction media have been realized in Japan [511]. Since 1985 Mitsubishi Gas Chemical [512] have been using direct carbonylation of *m*-xylene or pseudocumene to yield the corresponding aldehydes.

Further oxidation by air leads to trimellithic anhydride or pyromellithic dianhydride. It has been reported that 15,000 tons per year of trimellithic anhydride were produced by this process. Based on the same technology the acylation of 2-methylnaphthalene with CO and propene (1,000 tons per year) started in 1990 [513]. Air oxidation yields 2,6-naphthalene dicarboxylic acid which is of interest as an additive for PET bottle resins. Apart from these carbonylation reactions which have been already successfully implemented in industry, there are a number of carbonylation methods with good prospects of being realized in the near future. It is assumed that especially in the area of fine chemicals, new methods like amidocarbonylation, reductive carbonylation of nitro aromatics, and carbonylation of aryl-X will be commercialized for the first time. Moreover, methods already established will be

used for new substrates. Thus, CO chemistry will continue to fascinate both academic and industrial research and will be of economic benefit to society.

4. Outlook

Hydroformylation and carbonylation reactions will remain important processes for the manufacture of commodities and specialties. Parts of their molecules will be supplied by relatively inexpensive carbon monoxide or syngas. Therefore both processes will be competitive insofar as no alternative routes are available. While such competing processes are not within reach for relatively high-molecular oxo products, some reaction products of alternative low-molecular carbonylations may be available in the near future. Acetic acid, the most important carbonylation product, may be an example, which can be produced alternatively to the carbonylation routes from sludges [514] or from ethane by vapor-phase oxidation [515]. Since large capacities are involved (e.g. Hoechst Celanese Corp. with approx. 550,000 tons per year at one location) the economic consequences of such substitutions would be considerable, if the favourable economic predictions prove to be true.

The picture is more complex as regards hydroformylation processes. Taking four different possible trends as examples, which may be also apply to carbonylations, some developments may be in the offing:

On the one hand the world's demand for 'classical' oxo products (solvents, plasticizer and detergent alcohols) will be covered more and more by oxo plants in less developed countries by suitable resources (manpower and energy) [516]. Among other things this is the consequence of an uncritical licensing policy for years, which was supported by the high degree of automation. This automation reduced the demand for skilled personnel and make it possible for third-world countries – contrary to Biblical prophecy – to harvest the fruits of development from fields they did not themselves sow. In an interdependent global economy we have to live with the consequences of this fact: the loss of jobs.

Secondly (and following the general trend of chemical industry) the lost productions and jobs will be replaced by highly specialized manufacturing processes, which relate to the same chemical basis but involve more sophisticated process variants. So far the focal point of oxo research was the *regioselective* reaction control ('n/iso problem'). This will be replaced by a *stereoselective* control, which according to Takaya's breakthrough [247] will successfully be followed by the promising development of enantiomeric catalysts. Thus, highly sophisticated structures for pharmaceuticals and/or pesticides by asymmetric hydroformylation will be available, which otherwise would require costly multistep syntheses. There may be doubts as to use of the n/iso ratio of propylene hydroformylation as a measure of the excellence of oxo processes: the demand for isobutanal (for neopentyl glycol, methyl methacrylates, isobutyric acid etc) is now on the rise although the normal isomer has been in particular demand for decades. As far as carbonylations are concerned the enantiomeric syntheses will play the same role.

Thirdly the further development of complex catalysts will be a focal point of oxo and carbonylation research in future. As long as activity and selectivity controlling factors within the combination of central atoms and ligands have not fully been developed (or interpreted retrospectively) new experimental results may lead to new process variants. UCC's phosphites [75](c,d), bimetallic catalysts [517], or binuclear complexes in biphasic processes [93] are classical evidence of the chemistry as an experimental science.

Finally, process developments in both hydroformylation and carbonylation have not come to an end. The priority-claiming trend of the biphasic operation in oxo and carbonylation is remarkable, as demonstrated by the licensing of Ruhrchemie/Rhône-Poulenc's oxo process [133]. Aqueous systems as well as other biphasic or phase transfer systems follow the trend towards elegant, low-cost catalyst separation and thus the full exploitation of the advantages of homogeneous catalysis. On the other hand, process variants combining heterogeneous and homogeneous catalysis by 'heterogenization' of the homogeneous catalyst or catalyst precursors on supports (e.g. SLPC or SAPC techniques) were less successful and offer no promising chances: It is questionable whether the bonds between the central atoms of a hydroformylation or carbonylation catalyst and the bonding atoms of a support resist the manifold strains resulting from the multiple passage of the catalyst cycle. Strong bonds hamper the activity of the catalyst,

weak bonds cause 'leaching' of the catalyst metal. Additionally SAPC have to be adjusted within narrow water content limits, which is difficult to achieve [207].

Process variants include new proposals of simultaneous hydroformylation, aldolization, and hydrogenation of butenes [228], quite similar to Exxon's earlier Aldox process [227] (and in contrast to hydroformylation of butene and controlled aldolization of the C₅ aldehydes to C₁₀ intermediates [518]). As far as carbonylation is concerned Hoechst's one-step process to acetic acid *and* acetic anhydride would be the most advanced method, had too little economic courage on the part of management not prevented this progress and unique chance [102,519,520].

Carbonylation reactions will especially be a focal point of future work on the diversity of possible substrates and reaction products. As the immanent restriction for hydroformylations (feedstocks with double bonds) is not valid for carbonylation reactions, an abundance of starting materials will lead to many different products: conversions to profenes and their asymmetric variants, living ethylene/carbon monoxide copolymers, transfer of reductive or oxidative carbonylations to the industrial scale, tandem carbonylations, carbonylating couplings, the industrially significant amidocarbonylation, etc.

As in the case of hydroformylation and in addition to product-oriented work, fundamental research on *carbonylation catalysts* will be determinant in future: acceleration of Koch reaction systems by metallic co-catalysts, ligand-accelerated catalysis with phosphines, the arrangement of biphasic or phase-transfer catalyzed carbonylations, or the effect of different catalysts on the C–H activation of alkanes, aldehydes or other starting materials to a variety of products etc. As with hydroformylations the result of this work will provide a more comprehensive insight into carbonylation reactions.

References

- [1] J. Falbe (Ed.), *New Syntheses with Carbon Monoxide*, Springer, Berlin–Heidelberg–New York, 1980.
- [2] L. Markó, *J. Organomet. Chem.*, 245 (1983) 309; *ibid.*, 261 (1984) 485; *ibid.*, 283 (1985) 221; *ibid.*, 305 (1986) 333; *J. Organomet. Chem. Libr.*, 19 (1987) 271; *J. Organomet. Chem.*, 343 (1988) 399; *ibid.*, 357 (1989) 481; *ibid.*, 380 (1990) 429; *ibid.*, 404 (1991) 325.
- [3] R. Ugo, in W. Keim (Ed.), *Catalysis in C₁-Chemistry*, D. Reidel Publ. Comp., Dordrecht–Boston–Lancaster, 1983, p. 135.
- [4] P. Pino, *J. Organomet. Chem.*, 200 (1980) 223.
- [5] J.A. Moulijn, P.W.N.M. van Leeuwen, R.A. van Santen (Eds.), *Catalysis*, Elsevier, Amsterdam, 1993.
- [6] B. Cornils, W.A. Herrmann, M. Rasch, *Angew. Chem.*, 106 (1994) 2219; *Angew. Chem., Int. Ed. Engl.*, 33 (1994) 2144.
- [7] (a) L. Markó, F. Ungváry, *J. Organomet. Chem.*, 432 (1992) 1; (b) F. Ungváry, *J. Organomet. Chem.*, 457 (1993) 273.
- [8] (a) P.W.N.M. van Leeuwen, G. van Koten, *Stud. Surf. Sci. Catal.*, 79 (1993) 199 (b) Whyman, R., *Crit. Rep. Appl. Chem.*, 12 (1985) 128; (c) Murrer, B.A., M.J.H. Russell, *Catalysis*, 6 (1983) 169.
- [9] O. Roelen, *Lecture given at Chemische Werke Hüls*, Oct. 20 (1965) (inheritance O. Roelen).
- [10] B. Cornils, L. Markó in, *Methoden der organischen Chemie (Houben–Weyl)*, 4th Ed., Vol. E 18, Thieme, Stuttgart–New York, 1986, Part 2, p. 759.
- [11] D. Kirchhof, personal communication.
- [12] Chemische Verwertungsgesellschaft mbH, Oberhausen, (G. Schiller), DE 953.605 (1956), and Esso Res. Eng. Comp., GB 801.734 (1956).
- [13] R. Fowler, H. Connor, R.A. Baehl, *CHEMTECH*, (1976) 772; *Hydrocarbon Proc.*, 55(9) (1976) 247.
- [14] (a) J. Falbe (Ed.), *New Syntheses with Carbon Monoxide*, Springer, Berlin–Heidelberg–New York, 1980, p. 174 and e.g. Celanese Corp. (O.R. Hughes, M.E. Douglas), DE 2.125.382 (1970); (b) *Annual Report Celanese Corp.* 1974, p.9.
- [15] B. Cornils, W.A. Herrmann (Eds.), *Applied Homogeneous Catalysis by Organometallic Complexes*, VCH Verlag Chemie, Weinheim, 1996.
- [16] J. Haggin, *Chem. Eng. News*, Oct., 10 (1994) 28.
- [17] J. Manassen in, *Catalysis, Progress in Research*, (F. Basolo, R.I. Burwell, Eds.), Proc. NATO Science Committee Conf. on Catalysis, Santa Margherita di Pula, 1972, Plenum Press, New York, 1973, p. 177.
- [18] W. Keim, *Chem. Ing. Techn.*, 56 (1984) 850.
- [19] (a) W.S. Knowles, *Acc. Chem. Res.*, 16 (1983) 106; (b) W.S. Knowles, M.J. Sabacky, B.C. Vineyard, D.J. Weinkauff, *J. Am. Chem. Soc.*, 97 (1975) 2567.
- [20] (a) L. Cassar, *Chimica e l'Industria*, 67 (1985) No. 5, 256; (b) Montecatini Edison S.p.A. (M. Foa, L. Cassar, G. Chiusoli), DE 2.035.902 (1979).

- [21] (a) E. Wiebus, B. Cornils, *Chem. Ing. Techn.*, 66 (1994) 916, (b) *CHEMTECH*, 25 (1995) 33.
- [22] B. Cornils in, *New Syntheses with Carbon Monoxide* (Ed., J. Falbe), Springer-Verlag, Berlin–Heidelberg–New York 1980.
- [23] CAS Online Research (Feb. 1995), Keywords: Hydroformylation, Hydrocarbonylation.
- [24] P. Kalk, Y. Peres, J. Jenck, *Adv. Organomet. Chem.*, 32 (1991), 121.
- [25] F.P. Pruchnik, *Organometallic Chemistry of Transition Elements*, Plenum Press, New York 1990, p. 691.
- [26] H. Bahrmann, H. Bach in, *Ullmann's Encycl. Ind. Chem.*, 5th Ed. 1991, Vol. A 18, 321, VCH, Weinheim.
- [27] (a) G.K.I. Magomedov, L.V. Morozova, *Zh. Obsch. Khim.*, 51 (1981) 2266. (b) E.R. Tucci, *Ind. Eng. Chem. Prod. Res. Dev.*, 25 (1986) 27; *Chem. Abstr.*, 104 (1986) 111.757.
- [28] T.E. Nalesnik, J.H. Freudenberger, M. Orchin, *J. Organomet. Chem.*, 236 (1982) 95.
- [29] (a) A. Fusi, E. Cesarotti, R. Ugo, *J. Mol. Catal.*, 10 (1981) 213. (b) B.H. Chang, P.C. Coil, M.J. Brown, K.W. Barnett, *J. Organomet. Chem.*, 270 (1984) C23. (c) Z. He, N. Lugaan, D. Neibecker, R. Methieu, J.J. Bonnet, *J. Organomet. Chem.*, 426 (1992) 247.
- [30] (a) Review: R.A. Sanchez-Delgado, M. Rosales, M.A. Esteruelas, L.A. Oro, *J. Mol. Catal. A, Chemical*, 96 (1995) 231. (b) R.A. Sanchez-Delgado, A. Andriollo, N. Valencia, *J. Chem. Soc., Chem. Commun.* (1983) 444.
- [31] L.A. Oro, M.T. Pinillos, M. Royo, E. Pastor, *J. Chem. Res. Synop.*, (1984) 206; *Chem. Abstr.*, 101 (1984) 191.096.
- [32] L. Kaden, B. Lorenz, M. Wahren, *J. Prakt. Chem.*, 328 (1986) 407.
- [33] L. Alvila, T.A. Pakkanen, T.T. Pakkanen, O. Krause, *J. Mol. Catal.*, 73 (1992) 325.
- [34] M. Orchin, *Acc. Chem. Res.*, 14 (1981) 259.
- [35] B. Cornils, W.A. Herrmann, C.W. Kohlpaintner, *Nachr. Chem. Tech. Lab.*, 41 (1993) 544.
- [36] (a) L. Marko, *Fundam. Res. Homogeneous Catal.*, 4 (1984), 1; *Chem. Abstr.*, 100 (1984) 138.221. (b) F. Piacenti, M. Bianchi, P. Frediani, G. Menchi, U. Matteoli, *J. Organomet. Chem.*, 417 (1991) 77.
- [37] F. Heck, D.S. Breslow, *J. Am. Chem. Soc.*, 83 (1961) 4023.
- [38] (a) F. Ungvary, L. Marko, *Organometallics*, 2 (1983) 1608; (b) M.F. Mirbach, *J. Organomet. Chem.*, 265 (1984) 205; (c) M.F. Mirbach, *Inorg. Chim. Acta*, 88 (1984) 209. (d) J. Azran, M. Orchin, *Organometallics*, 3 (1984) 197; (e) I. Kovacs, F. Ungvary, L. Marko, *Organometallics*, 5 (1986) 209.
- [39] M. Orchin, *Ann. N.Y. Acad. Sci.*, 415 (1983) 129.
- [40] (a) G. Fachinetti, L. Balocchi, F. Secco, M. Venturini, *Angew. Chem.*, 93 (1981) 215; *Angew. Chem. Int. Ed. Engl.*, 20 (1981) 204. (b) P. Bradamante, A. Stefani, G. Fachinetti, *J. Organomet. Chem.*, 266 (1984) 303. (c) P. Pino, A. Major, F. Spindler, R. Tannenbaum, G. Bor, I.T. Horvath, *J. Organomet. Chem.*, 417 (1991) 65.
- [41] (a) F. Ungvary, L. Marko, *Organometallics*, 1 (1982) 1120. (b) Y. Matsui, M. Orchin, *J. Organomet. Chem.*, 244 (1983) 369. (c) Y. Matsui, M. Orchin, *J. Organomet. Chem.*, 246 (1983) 57.
- [42] (a) M.J. Mirbach, M.F. Mirbach, A. Saus, N. Topalsavoglou, T.N. Phu, *J. Am. Chem. Soc.*, 103 (1981) 7590. (b) M.J. Mirbach, M.F. Mirbach, A. Saus, N. Topalsavoglou, T.N. Phu, *J. Am. Chem. Soc.*, 103 (1981) 7594. (c) M.J. Mirbach, N. Topalsavoglou, T.N. Phu, M.F. Mirbach, A. Saus, *Chem. Ber.*, 116 (1983) 1422. (d) S. Mori, S. Tatsumi, M. Yasuda, K. Kudo, N. Sugita, *Bull. Chem. Soc. Jpn.*, 64 (1991) 3017.
- [43] (a) A.D. Harley, G.J. Guskey, G.L. Geoffroy, *Organometallics*, 2 (1983) 53. (b) C. Mahe, H. Patin, J.-Y. Le Marouille, A. Benoit, *Organometallics*, 2 (1983) 1051. (c) A. Ceriotti, L. Garlaschelli, G. Longoni, M.C. Malatesta, D. Strumolo, A. Fumagalli, S. Martinengo, *J. Mol. Catal.*, 24 (1984) 309. (d) S. Xue, Y. Luo, H. Fu, Y. Yin, *Ranliao Huaxue Xuebao*, 14 (1986) 354; *Chem. Abstr.*, 107 (1987) 9264. (e) T. Hayashi, Z.H. Gu, T. Sakakura, M. Tanaka, *J. Organomet. Chem.*, 352 (1988) 373. (f) W. Dai, H. Guo, R. Jiang, Q. Zhou, W. Wei, *Shiyou Huagong*, 17 (1988) 707; *Chem. Abstr.*, 110 (1989) 233.576. (g) J. Evans, G. Jingxing, H. Leach, A.C. Street, *J. Organomet. Chem.*, 372 (1989) 61. (h) A.R. El'man, V.I. Kurkunin, E.V. Slivinskii, S.M. Loktev, *Neftekhimiya*, 30 (1990) 46; *Chem. Abstr.*, 112 (1990) 197.383.
- [44] D.T. Brown, T. Eguchi, B.T. Heaton, J.A. Iggo, R. Whyman, *J. Chem. Soc., Dalton Trans.* (1991) 677.
- [45] (a) M. Garland, *Organometallics* (1993), 12, 535. (b) C. Fyhr, M. Garland, *Organometallics*, 12 (1993) 1753.
- [46] (a) M.G. Richmond, M. Absi-Halbi, C.U. Pittman, Jr., *J. Mol. Catal.*, 22 (1984) 367. (b) M. Hidai, A. Fukuoka, Y. Koyasu, Y. Uchida, *J. Chem. Soc., Chem. Commun.* (1984), 516. (c) G. Süß-Fink, G. Herrmann, *J. Chem. Soc., Chem. Commun.* (1985), 735. (d) M. Hidai, A. Fukuoka, Y. Koyasu, Y. Uchida, *J. Mol. Catal.*, 35 (1986) 29. (e) D. Li, W. Zhai, Z. Chen, Y. Sun, X. Zhao, Z. Wang, *Huaxue Xuebao*, 14 (1986) 990; *Chem. Abstr.*, 107 (1987) 28819. (f) M. Hidai, H. Matsuzaka, *Polyhedron*, 7 (1988) 2369. (g) M.G. Richmond, *J. Mol. Catal.*, 54 (1989) 199. (h) Y. Yin, F. Jiao, L. Qu, F. Nie, *Huaxue Xuebao*, 18 (1990) 38; *Chem. Abstr.*, 113 (1990) 193859. (i) M.-J. Don, M.G. Richmond, *J. Mol. Catal.*, 73 (1992) 181.
- [47] I.T. Horvath, M. Garland, G. Bor, P. Pino, *J. Organomet. Chem.*, 358 (1988) C17.
- [48] L.N. Lewis, *Chem. Rev.*, 93 (1993) 2693.
- [49] S.A. Laneman, F.R. Fronczek, G.G. Stanley, *J. Am. Chem. Soc.*, 110 (1988) 5585.
- [50] (a) S.A. Laneman, G.G. Stanley, *Adv. Chem. Ser.*, 230 (1992) 349. (b) M.E. Broussard, B. Juma, S.G. Train, W.-J. Peng, S.A. Laneman, G.G. Stanley, *Science*, 260 (1993) 1784. (c) Louisiana State Univ. (G.G. Stanley, S.C. Laneman), US 5.200.539 (1993).
- [51] G. Süß-Fink, *Angew. Chem.*, 106 (1994) 71; *Angew. Chem. Int. Ed. Engl.*, 33 (1994) 67.

- [52] (a) P. Kalck, J.M. Frances, P.M. Pfister, T.G. Southern, A. Thorez, *J. Chem. Soc., Chem. Commun.* (1983), 510. (b) P. Escaffre, A. Thorez, P. Kalck, B. Besson, R. Perron, Y. Colleuille, *J. Organomet. Chem.*, 302 (1986) C17. (c) A. Dedieu, P. Escaffre, J.M. Frances, P. Kalck, A. Thorez, *New J. Chem.*, 10 (1986) 631. (d) P. Kalck, Y. Peres, R. Queau, J. Molinier, P. Escaffre, E. Leandro de Oliveira, B. Peyrille, *J. Organomet. Chem.*, 426 (1992) C16.
- [53] R. Davis, J.W. Epton, T.G. Southern, *J. Mol. Catal.*, 77 (1992) 159.
- [54] (a) D. Cruz-Garritz, B. Rodriguez, H. Torrens, J. Leal, *Transition Met. Chem.*, 9 (1984) 284. (b) R.M. Catala, D. Cruz-Garritz, A. Hills, D.L. Hughes, R.L. Richards, P. Sosa, P. Terreros, H. Torrens, *J. Organomet. Chem.*, 359 (1989) 219. (c) C. Claver, A.M. Masdeu, N. Ruiz, C. Foces-Foces, F.H. Cano, M.C. Apreta, L.A. Oro, J. Garcia-Alejandre, H. Torrens, *J. Organomet. Chem.*, 398 (1990) 177.
- [55] (a) J.C. Bayon, P. Esteban, J. Real, C. Claver, A. Ruiz, *J. Chem. Soc., Chem. Commun.* (1989), 1056. (b) A. Polo, C. Claver, S. Castillon, A. Ruiz, J.C. Bayon, J. Real, C. Mealli, D. Masi, *Organometallics*, 11 (1992) 3525. (c) A. Polo, E. Fernandez, C. Claver, S. Castillon, *J. Chem. Soc., Chem. Commun.* (1992), 639.
- [56] A. Aaliit, A.M. Masdeu, A. Ruiz, C. Claver, *J. Organomet. Chem.*, 489 (1995) 101.
- [57] (a) A.M. Masdeu, A. Orejon, A. Ruiz, S. Castillon, C. Claver, *J. Mol. Catal.*, 94 (1994) 149. (b) C. Claver, S. Castillon, N. Ruiz, G. Delogu, D. Fabbri, S. Gladiali, *J. Chem. Soc., Chem. Commun.* (1993) 1833.
- [58] *Homogeneous Catalysis with Metal Phosphine Complexes* (Ed., L.H. Pignolet), Plenum Press, London (1983).
- [59] (a) BASF AG, (H.-J. Kneuper, M. Roeper, R. Paciello), DE 4.230.871 (1992); *Chem. Abstr.*, 120 (1994) 322.750. (b) BASF AG, (H.-J. Kneuper, M. Roeper, R. Paciello), *Eur. Pat. EP 0.588.225* (1994); *Chem. Abstr.*, 120 (1994) 322.751.
- [60] M. Polievka, A. Jegorov, L. Uhlar, V. Macho, *Collect. Czech., Chem Commun.*, 49 (1984) 1677; *Chem. Abstr.*, 101 (1984) 229.940.
- [61] (a) H. Schumann, H. Hemling, V. Ravindar, Y. Badrieh, J. Blum, *J. Organomet. Chem.*, 469 (1994) 213. (b) R. Uson, L.A. Oro, M.T. Pinillos, M. Royo, E. Pastor, *J. Mol. Catal.*, 14 (1982) 375. (c) P. Kalck, A. Thorez, M.T. Pinillos, L.A. Oro, *J. Mol. Catal.*, 31 (1985) 311.
- [62] J.T. Carlock, *Tetrahedron*, 40 (1984) 185.
- [63] (a) Hoechst AG (W.A. Herrmann, M. Elison, C. Köcher, J. Fischer, K. Öfele), DE Appl. 4.447.066 (1995) (b) Hoechst AG (W.A. Herrmann, M. Elison, C. Köcher, J. Fischer), DE Appl. 4.447.067 (1995), (c) Hoechst AG (W.A. Herrmann, J. Fischer, M. Elison, C. Köcher), DE Appl. 4.447.068 (1995); (d) Hoechst AG (W.A. Herrmann), DE Appl. 4.447.070 (1995).
- [64] (a) A.J. Arduengo, R.L. Harlow, M. Kline, *J. Am. Chem. Soc.*, 113 (1991) 361. (b) D.A. Dixon, A.J. Arduengo, *J. Phys. Chem.*, 95 (1991) 4180. (c) A.J. Arduengo, H.V. Rasika-Diaz, R.L. Harlow, M. Kline, *J. Am. Chem. Soc.*, 114 (1992) 5530.
- [65] (a) C.A. Tolman, W.C. Seidel, L.W. Gosser, *J. Am. Chem. Soc.*, 96 (1974) 53. (b) C.A. Tolman, *Chem. Rev.*, 77 (1977) 313.
- [66] A.A. Oswald, D.E. Hendriksen, R.V. Kastrup, K. Irikura, E.J. Mozeleski, D.A. Young, *Phosph. Sulfur*, 30 (1987) 237.
- [67] P.B. Dias, M.E. Minas de Piedade, J.A.M. Simoes, *Coord. Chem. Rev.*, 135/136 (1994) 737.
- [68] (a) C.P. Casey, G.T. Whitecker, *Isr. J. Chem.*, 30 (1990) 299. (b) C.P. Casey, G.T. Whitecker, C.F. Campana, D.R. Powell, *Inorg. Chem.*, 29 (1990) 3376. (c) C.P. Casey, G.T. Whitecker, M.G. Melville, L.M. Petrovich, J.A. Gavney Jr., D.R. Powell, *J. Am. Chem. Soc.*, 114 (1992) 5535.
- [69] (a) W.A. Herrmann, C.W. Kohlpaintner, E. Herdtweck, P. Kiprof, *Inorg. Chem.*, 30 (1991) 4271. (b) K. Yamamoto, S. Momose, M. Funahashi, S. Ebata, H. Ohmura, H. Komatsu, M. Miyazawa, *Chem. Lett.* (1994) 189. (c) W.A. Herrmann, R. Schmid, C.W. Kohlpaintner, T. Priermeier, *Organometallics*, 14 (1995) 1961
- [70] (a) A.A. Oswald, D.E. Hendriksen, R.V. Kastrup, E.J. Mozeleski, *Adv. Chem. Ser.*, 230 (1992) 395. (b) T.V. RajanBabu, T.A. Ayers, *Tetrahedron Lett.*, 35 (1994) 4295.
- [71] (a) O.R. Hughes, D.A. Young, *J. Am. Chem. Soc.*, 103 (1981) 6636. (b) J.D. Unruh, J.R. Christenson, *J. Mol. Catal.*, 14 (1982) 19. (c) J.D. Unruh, J.R. Christenson, O.R. Hughes, D.A. Young in *Chem. Ind., Catalysis of Organic Reactions* (Ed., W.R. Moser), Vol. 5, Marcel Dekker, New York, 1981, 309.
- [72] (a) M. Kranenburg, P.C.J. Kramer, P.W.N.M. van Leeuwen, *Organometallics* (1995), in press (b) Hoechst AG (W.A. Herrmann, C.W. Kohlpaintner, R. Schmid, G.P. Albanese, H. Bahrmann), DE 4.426.577 (1994).
- [73] (a) Tasoh Corp. (M. Oguri, T. Noda), JP 06.166.654 (1994); *Chem. Abstr.*, 121 (1994) 230.335. (b) Kuraray Co. (H. Saito, Y. Tokito), JP 06.135.888 (1994); *Chem. Abstr.*, 121 (1994) 204.837.
- [74] (a) P.W.N.M. van Leeuwen, C.F. Roobeek, *J. Organomet. Chem.*, 258 (1983) 343. (b) A. Polo, J. Real, C. Claver, S. Castillon, J.C. Bayon, *J. Chem. Soc., Chem. Commun.* (1990), 600. (c) A. van Rooy, E.N. Orij, P.C.J. Kamer, F. van den Aardweg, P.W.N.M. van Leeuwen, *J. Chem. Soc., Chem. Commun.* (1991), 1096. (d) T. Jongasma, G. Challa, P.W.N.M. van Leeuwen, *J. Organomet. Chem.*, 421 (1991) 121.
- [75] (a) D.R. Bryant, E. Billig, 4th Int. Conf. Chem. Plat. Group Met. (1990). (b) Union Carbide Corp. (E. Billig, A.G. Abatjoglou, D.R. Bryant), *Eur. Pat. Appl. EP 0.213.639* (1987); *Chem. Abstr.*, 107 (1987) 7392. (c) UCC (E. Billig, A.G. Abatjoglou, D.R. Bryant), *EP Appl. EP 0.214.622* (1987); *Chem. Abstr.*, 107 (1987) 25126. (d) UCC (E. Billig, A.G. Abatjoglou, D.R. Bryant), *US 4.769.498* (1988); *Chem. Abstr.*, 111 (1989) 117.287. (e) UCC (J.M. Maher, J.E. Babin, E. Billig, D.R. Bryant, T.W. Leung), *US 5.288.918* (1994); *Chem. Abstr.*, 121 (1994) 56996.
- [76] A. van Rooy, E.N. Orij, P.C.J. Kamer, P.W.N.M. van Leeuwen, *Organometallics*, 14 (1995) 34.
- [77] P.W.N.M. van Leeuwen, G.J.H. Buisman, A. van Rooy, P.C.J. Kamer, *Recl. Trav. Chim. Pays-Bas*, 113 (1994) 61.
- [78] BASF AG, (M. Roeper, P.M. Lorz, D. Koeffler), DE 4.204.808 (1993); *Chem. Abstr.*, 120 (1994) 133.862.

- [79] (a) C. Bergounhou, D. Neibecker, R. Reau, *J. Chem. Soc., Chem. Commun.* (1988), 1370. (b) D. Neibecker, R. Reau, *J. Mol. Catal.*, 53 (1989) 219. (c) D. Neibecker, R. Reau, *J. Mol. Catal.*, 57 (1989) 153. (d) D. Neibecker, R. Reau, *Angew. Chem.*, 101 (1989) 479. (e) D. Neibecker, R. Reau, S. Lecolier, *J. Org. Chem.*, 54 (1989) 5208. (f) D. Neibecker, R. Reau, *New J. Chem.*, 15 (1991) 279.
- [80] J. Hjortkjaer, P. Toromanova-Petrova, *J. Mol. Catal.*, 50 (1989) 203.
- [81] C.D. Wood, P.E. Garrou, *Catal. Conv. Synth. Gas Alcohols Chem. (Proc. Symp.)* (1984), 203; *Chem. Abstr.*, 101 (1984) 74726.
- [82] (a) Hoechst AG (H. Bahrmann, W.A. Herrmann, C.W. Kohlpaintner, R.B. Manetsberger), DE 4.220.267 (1993); *Chem. Abstr.*, 120 (1994) 218.184. (b) W.A. Herrmann, C.W. Kohlpaintner, R.B. Manetsberger, H. Bahrmann, H. Kottmann, *J. Mol. Catal.*, 97 (1995) 65.
- [83] K. Tamao, H. Yamamoto, H. Matsumoto, N. Miyake, T. Hayashi, M. Kumada, *Tetrahedron Lett.*, 16 (1977) 1389.
- [84] (a) all patents from Eastman Kodak (T.J. Devon, G.W. Phillips, T.A. Puckette, J.L. Stavinoha, J.J. Vanderbilt), PCT Int. Appl. WO 87/07 600 (1987); *Chem. Abstr.*, 109 (1988) 8397. (b) T.J. Devon, G.W. Phillips, T.A. Puckette, J.L. Stavinoha, J.J. Vanderbilt, US 4.694.109 (1987); *Chem. Abstr.*, 108 (1988) 7890. (c) T.A. Puckette, T.J. Devon, G.W. Phillips, J.L. Stavinoha, US 4.879.416 (1989); *Chem. Abstr.*, 112 (1990) 217.269. (d) J.L. Stavinoha, G.W. Phillips, T.A. Puckette, T.J. Devon, EP EP 0.326.286 (1989); *Chem. Abstr.*, 112 (1990) 98.823.
- [85] (a) Easrman Kodak (T.J. Devon, G.W. Phillips, T.A. Puckette; J.L. Stavinoha, J.J. Vanderbilt), US 5.332.846 (1994); *Chem. Abstr.*, 121 (1994) 280.879. (b) Hoechst AG (W.A. Herrmann, R.B. Manetsberger, G.P. Albanese, H. Bahrmann, P. Lappe), DE 4.333.307 (1994). (c) J.D. Unruh, personal communication (1995).
- [86] (a) F.A. Cotton, B. Hong, *Progress Inorg. Chem.*, 40 (1992) 179. (b) H.A. Mayer, W.C. Kaska, *Chem. Rev.*, 94 (1994) 1239.
- [87] G. Kiss, I.T. Horváth, *Organometallics*, 10 (1991) 3798.
- [88] (a) T. Onoda, *CHEMTECH*, 23 (9) (1993) 34. (b) K. Sato, C. Miyazawa, K. Wada, T. Onoda, *Nippon Kagaku Kaishi* (1994), 681; *Chem. Abstr.*, 121 (1994) 136.524.
- [89] (a) C. Abu-Gnim, I. Amer, *J. Chem. Soc., Chem. Commun.*, 115; (1994) (b) C. Basoli, C. Botteghi, M.A. Cabras, G. Chelucci, M. Marchetti, *J. Organomet. Chem.*, 488 (1995) C20.
- [90] (a) A. Bader, E. Lindner, *Coord. Chem. Rev.*, 108 (1991) 27. (b) C. Vaecher, A. Mortreux, F. Petit, J.P. Picaret, H. Sliwa, N.W. Murall, A.J. Welch, *Inorg. Chem.*, 24 (1985) 2338. (c) S. Gladiali, L. Pinna, C.G. Arena, E. Rotondo, F. Faraone, *J. Mol. Catal.*, 66 (1991) 183. (d) D. Drommi, F. Nicolo, C.G. Arena, G. Bruno, F. Faraone, R. Gobetto, *Inorg. Chim. Acta*, 221 (1994) 109. (e) G.R. Newkome, *Chem. Rev.*, 93 (1993) 2067. (f) S. Naili, J.-F. Carpentier, F. Agbossou, A. Mortreux, G. Nowogrocki, J.-P. Wignacourt, *Organometallics*, 14 (1995) 401. (g) P.A.T. Hoye, R.D.W. Kemmit, D.L. Law, *Appl. Organomet. Chem.*, 7 (1993) 513. (h) C. Abu-Gnim, I. Amer, *J. Mol. Catal.*, 85 (1993) L275.
- [91] (a) P.W.N.M. van Leeuwen, C.F. Roobeck, R.L. Wife, J.H.G. Frijns, *J. Chem. Soc., Chem. Commun.* (1986), 31. (b) P.W.N.M. van Leeuwen, C.F. Roobeck, *New J. Chem.*, 14 (1990) 487. (c) P.W.N.M. van Leeuwen, C.F. Roobeck, J.H.G. Frijns, *Organometallics*, 9 (1990) 1211.
- [92] M. Matsumoto, M. Tamura, *J. Mol. Catal.*, 19 (1983) 365.
- [93] (a) W.A. Herrmann, C.W. Kohlpaintner, *Angew. Chem.*, 105 (1993) 1588; *Angew. Chem. Int. Ed. Engl.*, 32 (1993) 1524. (b) P. Kalck, F. Monteil, *Adv. Organomet. Chem.*, 34 (1992) 219.
- [94] W.A. Herrmann, G.P. Albanese, R.B. Manetsberger, H. Bahrmann, P. Lappe, *Angew. Chem.*, 107 (1995) 893; *Angew. Chem. Int. Ed. Engl.*, 34 (1995) 811.
- [95] (a) T. Bartik, B. Bartik, I. Guo, B.E. Hanson, *J. Organomet. Chem.*, 480 (1994) 15. (b) H. Ding, B.E. Hanson, T. Bartik, B. Bartik, *Organometallics*, 13 (1994) 3761. (c) T. Bartik, B. Bartik, B.E. Hanson, *J. Mol. Catal.*, 88 (1994) 43. (d) H. Ding, B.E. Hanson, *J. Chem. Soc., Chem. Commun.* (1994), 2747. (e) H. Ding, B.E. Hanson, T.E. Glass, *Inorg. Chim. Acta*, 229 (1995) 329.
- [96] (a) E. Fache, F. Senocq, C. Santini, J.-M. Basset, *J. Chem. Soc., Chem. Commun.* (1990), 1776. (b) E. Fache, C. Santini, F. Senocq, J.-M. Basset, *J. Mol. Catal.*, 72 (1992) 337.
- [97] (a) R.A. Dubois, P.E. Garrou, K. Lavin, H.R. Allock, *Organometallics*, 3 (1984) 649. (b) A.G. Abatjoglou, E. Billig, D.R. Bryant, *Organometallics*, 3 (1984) 923. (c) A.G. Abatjoglou, D.R. Bryant, *Organometallics*, 3 (1984) 932. (d) R.M. Deshpande, S.S. Divekar, R.V. Gholap, R.V. Chaudhari, *J. Mol. Catal.*, 67 (1991) 333.
- [98] *Chemische Verwertungsgesellschaft Oberhausen* (A. Gemassmer et al.), DE 896.341 (1953) and DE 902.491 (1954).
- [99] S.L. Regen, *Angew. Chem.*, 91 (1979) 464.
- [100] Montecatini Edison S.p.A. (M. Foa, L. Cassar, G.P. Chiusoli), DE 2.035.902 (1979).
- [101] e.g. L.W. Grosser, H.W. Knoth, G.W. Parshall, *J. Mol. Catal.*, 2 (1977) 253.
- [102] Hoechst AG (H. Bahrmann, M. Haubs, W. Kreuder, T. Müller), EP 0.374.615 (1989).
- [103] Exxon Chemical Patents Inc. (F.J. Healy, J.R. Livingston, E.J. Mozeleski, J.G. Stevens, G. Sartori), US 5.298.669 (1993); US 5.288.818 (1991), WO 9304049 (1993).
- [104] J. Falbe, H. Bahrmann, *Chemie in unserer Zeit*, 15 (1991) 37.
- [105] G.W. Parshall, *J. Am. Chem. Soc.*, 94 (1972) 8716.
- [106] C. Larpent, H. Patin, *J. Mol. Catal.*, 44 (1988) 191.
- [107] see e.g. patents of Mitsubishi Chem. (DE 2.302.962), Showa Denko KK (DE 2.535.597), Phillips Petroleum Comp. (US 4.068.054, US 3.995.097, US 3.956.257), Chisso Corp. (DE 1.904.815), or Ruhrchemie AG (DE 1.195.496).
- [108] B. Heinrich, J. Hjortkjaer, A. Nikitidis, C. Andersson, *J. Mol. Catal.*, 81 (1993) 333.

- [109] B. Gronewold, D. Hesse, *Chem. Ing. Tech.*, 67 (1995) 82.
- [110] F. J6o, M.T. Beck, *J. Mol. Catal.*, 24 (1984) 135.
- [111] T.G. Southern, *Polyhedron*, 8(4) (1989) 407.
- [112] B. Cornils, *Nachr. Chem. Tech. Lab.*, 42 (1994) 1136.
- [113] R.V. Chaudhari, A. Bhattacharya, B.M. Bhanage, Paper presented to the Symposium, *Catalysis in Multiphase Reactors*, Lyon/France, Dec. (1994).
- [114] Z.M. Michalska, D.E. Webster, *Platinum Met. Rev.*, 18 (1974) 65.
- [115] F. J6o, Z. T6th, *J. Mol. Catal.*, 8 (1980) 369.
- [116] (a) W.A. Herrmann, C.W. Kohlpaintner, H. Bahrman, W. Konkol, *J. Mol. Catal.*, 73 (2) (1992) 191.
- [117] S. Ahrland, J. Chatt, N.R. Davies, A.A. Williams, *J. Chem. Soc.*, 276 (1958) 276.
- [118] F. Joo, M. Beck, *React. Kinetics and Catal. Lett.* (1975), 275; Paper presented to the Symposium, *Rhodium in Homogeneous Catalysis*, Veszpr6m/Hungary, Sept. 1978, Proceedings, p. 51.
- [119] A.F. Borowski, D.J. Cole-Hamilton, G. Wilkinson, *Nouv. J. Chem.*, 2 (1978) 137.
- [120] T. Jarol6m, J. Podlahov6, J., *J. Inorg. Nucl. Chem.*, 38(1) (1976) 125.
- [121] (a) R.T. Smith, R.K. Ungar, M.C. Baird, *Trans. Met. Chem.*, 6 (1981) 197; (b) *ibid.*, 7 (1982) 288; (c) *Organometallics*, 2 (1983) 1138.
- [122] J. Chatt, G.J. Leigh, R.M. Slade, *J. Chem. Soc. Dalton Trans.* (1973), 2021.
- [123] L.D. Pettit, H.M.N.H. Irving, *J. Chem. Soc.* (1964), 5336.
- [124] Rh6ne-Poulenc Ind. (E. Kuntz et al.), FR 2.230.654 (1983), FR 2.314.910 (1975), FR 2.338.253 (1976), FR 2.349.562 (1976), FR 2.366.237 (1976), FR 2.473.504 (1979), FR 2.478.078 (1980), FR 2.550.202 (1983), FR 2.561.650 (1984); DE 2.627.354 (1976).
- [125] E. Kuntz, *CHEMTECH*, 17(9) (1987) 570.
- [126] O. Herd, K.P. Langhans, O. Steltzer, N. Weferling, W.S. Sheldrick, *Angew. Chem.*, 105 (1993) 1097.
- [127] Z. Wang, G. Yuan, Q. Zhou, *Shiyou Huagong*, 16(10) (1987) 691; *Chem. Abstr.* 109: 109.832.
- [128] Union Carbide, (A.G. Abatjoglou, D.R. Bryant, R.R. Peterson), EP 0.350.922 (1990).
- [129] (a) B. Cornils et al., 4th Int. Symp. on Homog. Catal. Leningrad (1984), Proceedings, p. 487; *Int. Symp. High-Pressure Chem. Engng.*, Erlangen (1984), Preprints, p. 129; 1st IUPAC Symp. Org. Chem., Jerusalem (1986), Abstracts p. 295; (b) *Ruhrchemie AG*, DE 3.234.701, 3.235.029, 3.235.030, 3.412.335, 3.341.035, 3.431.643, 3.412.336, 3.443.474, 3.511.428, 3.546.123, 3.630.587, 3.640.614, 3.726.128 etc., filed between (1982) and (1994); (c) B. Cornils, E. Kuntz, *J. Organomet. Chem.*, (1995) in press.
- [130] H.W. Bach, H. Bahrman, W. Gick, W. Konkol, E. Wiebus, *Chem. Ing. Tech.*, 59 (1987) 882.
- [131] K.H. Schmidt, *Chem. Ind.*, 37 (1985) 762; A. Behr, M. Roeper, *Erd6l und Kohle-Erdgas-Petrochem.*, 37 (1984) 485.
- [132] A. Chauvel, B. Delmon, W.F. H6lderich, *Appl. Catal. A, General*, 115 (1994) 173.
- [133] *European Chem. News*, Jan. 15 (1995) 29; *Europa-Chemie*, (1) (1995) 10.
- [134] Hoechst AG (W.A. Herrmann, C.W. Kohlpaintner, H. Bahrman et al.), EP 0.477.747 (1991), 0.491.240 (1991), 0.571.819 (1993), 0.575.785 (1993), and DE 3.840.600 (1988).
- [135] B.E. Hanson et al., *Inorg. Chim. Acta*, 229 (1995) 329; *Organometallics.*, 12 (1993) 164; *Organometallics.* (1995), in press; *J. Mol. Catal.*, 88 (1994) 43.
- [136] NATO Advanced Research Workshop, *Aqueous Organometallic Chemistry and Catalysis*, Debrecen/Hungary, Aug./Sept. 1994, Preprints.
- [137] Y. Yan, H. Zhuo, Z. Jin, *Fenzi Cuihua*, 8(2) (1994) 147; *Chem. Abstr.* 121: 111.875.
- [138] F. Mercier, F. Mathey, *J. Organomet. Chem.*, 462 (1993) 103.
- [139] Y. Amrani, D. Sinou, *J. Mol. Catal.*, 24 (1984) 231.
- [140] Rh6ne-Poulenc Ind. (B. Besson, P. Kalck, A. Thorez), EPO. 420.169 (1985).
- [141] D. Sinou, *Bull. Soc. Chim. Fr.*, (1) (1987) 480.
- [142] P. Kalck, *Polyhedron*, 7 (1988) 2441.
- [143] B. Fell, G. Papadogianakis, *J. prakt. Chem./Chemiker-Ztg.*, 336 (1994) 591.
- [144] Johnson Matthey PLC. (M.J.H. Russel, B.A. Murrer), BE 890.210 (1982), FR 2.489.308 (1982).
- [145] R.S. Dickson, T. De Simone, E.M. Campi, W.R. Jackson, *Inorg. Chim. Acta*, 220 (1–2) (1994) 187.
- [146] J. Gao, C.T. Au, S. Wang, C. Yin, K.R. Tsai, *Fenzi Cuihua*, 4(1) (1990) 68.
- [147] Hoechst AG (H. Bahrman, E. Wiebus et al.), EP 0.562.450 and 0.562.451. (1993), EP 0.216.315 (1986), EP 0.576.905 (1993).
- [148] P.J. Quinn, C.E. Taylor, *J. Mol. Catal.*, 13 (1981) 389.
- [149] Exxon Chem. Patents Inc. (Suci, E., J.R. Livingston, E.J. Mozeleski), US 5.300.617 (1993).
- [150] Union Carbide (A.G. Abatjoglou, D.R. Bryant), US 4.731.486 (1986).
- [151] S.S. Divekar, R.M. Deshpande, R.V. Chaudhari, *Catal. Lett.*, 21 (1993) 191.
- [152] (a) A. Behr, W. Keim, *Erd6l, Erdgas, Kohle, Petrochem.*, 103 (1987) 126; (b) A. Behr, Paper presented on the occasion of Prof. Keim's 60th birthday, Aachen/Germany, Dec. 1994.
- [153] M. Roeper, Paper presented on the occasion of Prof. Keim's 60th birthday, Aachen/Germany, Dec. 1994.
- [154] Kuraray Co. (Y. Tokitoh, N. Yoshimura), US 4.808.756 (1989).

- [155] A. Behr, *Fat Sci. Technol.*, 92(10) (1990) 375.
- [156] Hoechst AG, (M. Beller, C.W. Kohlpaintner), DE 4.415.681 and 4.415.682 (1994).
- [157] L. Cassar in M. Tsutsui/R. Ugo, *Fundamental Research in Homogeneous Catalysis*, Plenum Press, New York/London, 1976, p. 115.
- [158] I. Willner, R. Maidan, *J. Chem. Soc., Chem. Commun.*, 13 (1988) 876.
- [159] J. Wu, G. Yuan, Q. Zhou, *Shiyou Huagong*, 20(2) (1991) 79; *Chem. Abstr.* 115: 321.659.
- [160] P. Purwanto, H. Delmas, Paper presented at the Symposium, *Catalysis in Multiphase Reactors*, Lyon/France, Dec. 1994.
- [161] S.S. Deshpande, Divekar, B.M. Bhanage, R.V. Chaudhari, *J. Mol. Catal.*, 75(1) (1992) L19.
- [162] Eniricerche S.p.A. (L. Tinucci, E. Platone), EP 0.380.154 (1990).
- [163] e.g. Ruhrchemie AG (B. Cornils, E. Wiebus et al.), DE 3.640.614 (1986).
- [164] Ruhrchemie AG (B. Cornils, W. Konkol, H.W. Bach, G. Dämbkes, W. Gick, W. Greb, E. Wiebus, H. Bahrmann), DE 3.413.427 (1984), DE 3.546.123 (1985).
- [165] Hoechst AG (B. Cornils, H. Bahrmann, E. Wiebus et al.), EP 0.158.246 (1984).
- [166] Rhône-Poulenc S.A. (E. Kuntz), DE 2.627.354 (1976).
- [167] Ruhrchemie AG, (B. Cornils, H. Bahrmann, W. Lipps, W. Konkol), EP 0.173.219 (1985), DE 3.511.428 (1985).
- [168] R. Chaudhari, B.M. Bhanage, R.M. Deshpande, H. Delmas, *Nature*, 373 (1995) 501.
- [169] G. Fremy, E. Montflier, J.-F. Carpentier, Y. Castanet, A. Mortreux, *Angew. Chem.* (1995), in press.
- [170] (a) I. Guo, B.E. Hanson, I. Toth, M.E. Davis, *J. Mol. Catal.*, 70 (1991) 363; (b) T. Bartik, B. Bartik, B.E. Hanson, *J. Mol. Catal.*, 85 (1993) 121.
- [171] F. J6o, E. Tr6csanyi, *J. Organometal. Chem.*, 231 (1982) 63.
- [172] C. Larpent, R. Dabard, H. Patin, *New J. Chem.*, 12 (1988) 907.
- [173] A. Lubineau, J. Aug6, Y. Queneau, *Synthesis*, 8 (1994) 741.
- [174] R.M. Deshpande, S.S. Divekar, B.M. Bhanage, R.V. Chaudhari, *J. Mol. Catal.*, 75 (1992) L19.
- [175] (a) Shell Oil Co. (W. Keim et al.), US 3.635.937, US 3.637.636, US 3.644.563, US 3.644.564, US 3.647.914, US 3.647.906, US 3.647.915, US 3.661.803 and US 3.686.159; all 1972; (b) (R.F. Mason) US 3.737.475 (1973).
- [176] I.T. Horv6th, J. R6bai, *Science*, 266 (1994) 72.
- [177] Exxon Res. Eng. Comp. (I.T. Horv6th, J. Rabai), EP 0.633.062 (1994).
- [178] P.A. Stevens, Paper presented to the, 7. Mikrosymposium, Bayer AG, Leverkusen, Oct. 5–7, 1994.
- [179] J.A. Gladysz, *Science*, 266 (1994) 55.
- [180] M. Vogt, Ph.D. Thesis, RWTH Aachen, Aug. 26, 1991.
- [181] Exxon Res. Eng. Comp. (I. Huang, R. Drogin), *Int. Pat. WO 80/01691*.
- [182] V. Schurig, Paper presented to the, *Symp. on Rhodium in Homogeneous Catalysis*, Veszprem/Hungary, Sept. 11–13, 1978, *Proceedings*, p. 140.
- [183] Sumitomo Chem. Co., (K. Nomura, M. Ishino), JP 04.266.863 (1991); *Chem. Abstr.* 118: 61.531.
- [184] Z. Jin, Y. Yan, H. Zuo, B. Fell, *J. Prakt. Chem./Chemiker-Ztg.*, (1995) in press.
- [185] D.E. Bergbreiter, Li Zhang, V.M. Mariagnanam, *J. Am. Chem. Soc.*, 115 (1993) 9295.
- [186] K.T. Wan, M.E. Davis, *Nature*, 370 (1994) 449.
- [187] J.M. Brown, S.G. Davies, *Nature*, 370 (1994) 418.
- [188] A. Behr, *Chem. Ing. Tech.*, 65 (1993) 568; *Fat Sci. Technol.*, 92(10) (1990) 375.
- [189] (a) D.C. Bailey, S.H. Langer, *Chem. Rev.*, 81 (1981) 109. (b) D.D. Whitehurst, *CHEMTECH*, 10 (1980) 44. (c) Y.I. Yermakov, B.N. Kuznetsov, V.A. Zakharov, *Stud. Surf. Sci. Catal.*, 8 (1981) 1. (d) F.R. Hartley, *Supported Metal Complexes*, Reidel, Dordrecht, 1985. (e) I.M. Campbell, *Catalysis at Surfaces*, Chapman and Hall, London, 1988.
- [190] C.U. Pittman, Jr., L.R. Smith, *J. Am. Chem. Soc.*, 97 (1975) 1949.
- [191] (a) C.U. Pittman, Jr. in, *Polymer-Supported Reactions in Organic Synthesis* (Eds., P. Hodge and D.C. Sherrington), Wiley, New York, 1980, p. 249. (b) C.U. Pittman, Jr. in, *Comprehensive Organometallic Chemistry* (Eds., G. Wilkinson, F.G. A Stone and E.W. Abel), Pergamon Press, Oxford, 1982, Vol. 8, p. 553.
- [192] J. Lieto, D. Milstein, R.L. Albright, J.V. Minkiewicz, B.C. Gates, *CHEMTECH*, 13 (1983) 46.
- [193] P. Kalck, E. Leandro de Oliveira, R. Queau, B. Peyrille, J. Molinier, *J. Organomet. Chem.*, 433 (1992) C4.
- [194] (a) K.S. Ro, S.I. Woo, *Appl. Catal.*, 69 (1991) 169. (b) K.S. Ro, S.I. Woo, *J. Catal.*, 145 (1994) 327.
- [195] (a) T. Jongsma, P. Kimkes, G. Challa, P.W.N.M. van Leeuwen, *Polymer*, 33 (1992) 161; (b) P.W.N.M. van Leeuwen, T. Jongsma, G. Challa, *Macromol. Symp.*, 80 (1994) 241.
- [196] M.J. Sundell, J.H. N6sman, *CHEMTECH*, 23 (1993) (12), 16.
- [197] (a) L.A. Gerritsen, A. van Meerkerk, M.H. Vreugdenhill, J.J.F. Scholten, *J. Mol. Catal.*, 9 (1980) 139. (b) L.A. Gerritsen, J.M. Herman, W. Klut, J.J.F. Scholten, *J. Mol. Catal.*, 9 (1980) 157. (c) L.A. Gerritsen, J.M. Herman, J.J.F. Scholten, *J. Mol. Catal.*, 9 (1980) 241. (d) L.A. Gerritsen, W. Klut, M.H. Vreugdenhill, J.J.F. Scholten, *J. Mol. Catal.*, 9 (1980) 257. (e) L.A. Gerritsen, W. Klut, M.H. Vreugdenhill, J.J.F. Scholten, *J. Mol. Catal.*, 9 (1980) 265. (f) N.A. de Munck, J.P.A. Notenboom, J.E. de Leur, J.J.F. Scholten, *J. Mol. Catal.* (1981), 11, 233. (g) H.L. Pelt, L.A. Gerritsen, G. van der Lee, J.J.F. Scholten, *Stud. Surf. Sci. Catal.*, 16 (1983) 369.

- [198] (a) J. Hjortkjaer, M.S. Scurrill, P. Simonsen, *J. Mol. Catal.*, 6 (1979) 405. (b) J. Hjortkjaer, M.S. Scurrill, P. Simonsen, H. Svendsen, *J. Mol. Catal.*, 12 (1981) 179.
- [199] (a) J.J.F. Scholten, R. van Hardeveld, *Chem. Eng. Commun.*, 52 (1987) 75; *Chem. Abstr.*, 107 (1987) 98563. (b) J.M. Herman, A.P.A.F. Rocourt, P.J. van den Berg, P.J. van Krugten, J.J.F. Scholten, *Chem. Eng. J.*, 35 (1987) 83; *Chem. Abstr.*, 107 (1987) 98567.
- [200] M.E. Davis, *CHEMTECH*, 22 (1992) 498.
- [201] J.P. Arhancet, M.E. Davis, J.S. Merola, B.E. Hanson, *Nature*, 339 (1989) 454.
- [202] (a) J.P. Arhancet, M.E. Davis, J.S. Merola, B.E. Hanson, *J. Catal.*, 121 (1990) 327. (b) I. Guo, B.E. Hanson, I. Toth, M.E. Davis, *J. Organomet. Chem.*, 403 (1991) 221. (c) I. Guo, B.E. Hanson, I. Toth, M.E. Davis, *J. Mol. Catal.*, 70 (1991) 363. (d) Y. Yuan, Y. Yang, H. Zhang, Q. Cai, *Gaodeng Xuexiao Huaxue Xuebao*, 14 (1993) 863; *Chem. Abstr.*, 120 (1994) 194.442.
- [203] E. Fache, C. Mercier, N. Pagnier, B. Despeyroux, P. Panster, *J. Mol. Catal.*, 79 (1993) 117.
- [204] J.P. Arhancet, M.E. Davis, B.E. Hanson, *Catal. Lett.*, 11 (1991) 129.
- [205] (a) T. Ishizaki, H. Kumobayashi, US 5.274.146 (1993). (b) K.T. Wan, M.E. Davis, *J. Chem. Soc., Chem. Commun.* (1993), 1262. (c) K.T. Wan, M.E. Davis, *Tetrahedron: Asymmetry*, 4 (1993) 2461.
- [206] (a) Y.Z. Yuan, Y.Q. Yang, J.L. Xu, H.B. Zhang, K.R. Tsai, *Chin. Chem. Lett.*, 5 (1994) 291; *Chem. Abstr.*, 121 (1994) 156.919. (b) H. Chen, H. Liu, Y. Li, P. Cheng, X. Li, *Fenzi Cuihua*, 8 (1994) 124; *Chem. Abstr.*, 121 (1994) 72.363. (c) H. Liu, H. Chen, Y. Li, P. Cheng, X. Li, *Fenzi Cuihua*, 8 (1994) 22; *Chem. Abstr.*, 120 (1994) 269.612. (d) Y. Yuan, A. Liu, Y. Yang, J. Xu, H. Zhang, Q. Cai, *Fenzi Cuihua*, 7 (1993) 439; *Chem. Abstr.*, 120 (1994) 298.017.
- [207] B.B. Bunn, T. Bartik, B. Bartik, W.R. Bebout, T.E. Glass, B.E. Hanson, *J. Mol. Catal.*, 94 (1994) 157.
- [208] R. Brusewitz, D. Hesse, *Dechema Monogr.*, 122 (1991) 283.
- [209] T. Onoda, *CHEMTECH* (9) (1993) 34.
- [210] (a) M. Misono, N. Nojiri, *Appl. Catalysis*, 64 (1990) 1; (b) N. Nojiri, M. Misono, *Appl. Catal. A, General*, 93 (1993) 103.
- [211] Ruhrchemie AG (B. Cornils, W. Konkol, H.W. Bach, W. Gick, E. Wiebus, H. Bahrman), DE 3.447.030 (1984) and EP 0.186.075 (1984).
- [212] Hoechst AG (H. Bahrman, B. Cornils, E. Wiebus et al.), EP 0.216.314 (1985), DE 2.833.538 (1978) and DE 2.837.480 (1978).
- [213] Rhône-Poulenc Ind., DE 2.627.354 (1976).
- [214] T. Bartik, B. Bartik, B.E. Hanson, I. Guo, I. Toth, *Organometallics*, 12 (1993) 164.
- [215] Yeda Research and Development Co. (J. Manassen, Y. Dror), US 4.415.500 (1983).
- [216] Hoechst AG (H. Bahrman, P. Lappe), EP 602.463 (1994).
- [217] Ruhrchemie AG (B. Cornils, W. Konkol, H. Bahrman, H.W. Bach, E. Wiebus), DE 3.411.034 (1984), 3.443.474 (1985), (H. Bahrman, J. Weber, H.W. Bach, L. Bexten), EP 0.216.315 (1986).
- [218] Hoechst AG, CN 85-105.102.
- [219] Y. Dror, J. Manassen, *Stud. Surf. Sci. Catal.*, 7 (1981) (Pt. B, New Horiz. Catal.) 887.
- [220] Johnson Matthey plc. (R.M.H. Russel, B.A. Murrer), GB 2.085.974 (1980), US 4.399.312 (1983), DE 3.135.127 (1990); M.J.H. Russel, *Chemie-Technik*, 17(6) (1988) 148.
- [221] G. Oehme, E. Paetzold, R. Selke, *J. Mol. Catal.*, 71 (1992) L1; *Tetrahedron*, 49 (1993) 6605; *Angew. Chem.*, 106 (1994) 2272; DD 259.194 (1987).
- [222] Y. Matsui, M. Orchin, *J. Organomet. Chem.*, 244 (1983) 369.
- [223] B. Fell, G. Papadogianakis, *J. Mol. Catal.*, 66 (1991) 143.
- [224] Hoechst AG (H. Bahrman, B. Fell, G. Papadogianakis), DE 3.942.954 (1989).
- [225] R.V. Chaudhari, B.M. Bhanage, R.M. Deshpande, H. Delmas, *Nature*, 373 (1995) 501.
- [226] M.J.H. Russel, *Platinum Metals Rev.*, 32 (1988) 179.
- [227] B. Cornils in Falbe (Ed.), *New Syntheses with Carbon Monoxide*, Springer, Berlin–Heidelberg–New York, 1980, p. 146.
- [228] Exxon Res. Engng. Comp., (I. Huang, R. Drogin), *Int. Pat. WO 80/01691* (1980).
- [229] Union Carbide Corp. (R.A. Fiato, R.L. Pruett), EP 0.026.998 (1980).
- [230] N. Nojiri, M. Misono, *Appl. Catal.*, A, 93 (1993) 103.
- [231] Kuraray Corp. (M. Matsumoto, M. Tamura et al.), US 4.215.077 (1980) and 4.567.305 (1986).
- [232] N. Yoshimura, M. Tamura in, *Successful Design of Catalysts*, (Inui, Ed.), Elsevier, Amsterdam, 1988, p. 307; N. Yoshimura et al., *Nippon Kagaku Kaishi* (2) (1993) 119.
- [233] Rhône-Poulenc (E. Kuntz), FP 2.366.237 (1976), DE 2.735.516 (1978).
- [234] Kuraray Corp. (N. Yoshimura, M. Tamura et al.), US 4.356.333 (1982), US 4.417.079 (1983), US 4.927.960 (1990), US 5.057.631 (1991), EP 0.287.066 (1988); EP 0.436.226 (1990), FR 2.499.978 (1982); GB 2.074.156 (1980).
- [235] BASF AG (M. Roeper, W. Bertleff, D. Koeffler), US 4.962.243 (1990) and US 5.043.487 (1991).
- [236] Mitsubishi Kasei, US 4.990.698 (1991).
- [237] Shell Oil Co., US 5.030.792 (1991).
- [238] Kuraray Co. (Tokitoh, Y., N. Yoshimura), US 4.808.756 (1989); JP 3.287.554 (1991); EP 0.088.955 (1983).
- [239] BASF AG (R. Kummer, D. Franz, H.P. Rath), EP 0.244.616 (1987).
- [240] Kuraray Co., (T. Kitamura, M. Matsumoto, M. Tamura), DE 3.210.617 (1981), *Chem. Abstr.*, 98 (1983) 106.821 g.

- [241] S.D. Burke, J.E. Cobb, *Tetrahedron Lett.*, 27(36) (1986) 4237.
- [242] I.T. Horváth, *Catal. Lett.*, 6 (1990) 43.
- [243] P. Escaffre, A. Thorez, P. Kalck, *New J. Chem.*, 11 (1987) 601; P. Kalck et al., *New J. Chem.*, 12 (1988) 687.
- [244] M. Barber, *Stereotechnology Pharm. Manuf. Int.* (1990), 137.
- [245] Recent Reviews: (a) C. Botteghi, S. Paganelli, A. Schionato, M. Marchetti, *Chirality*, 3 (1991) 355. (b) J.K. Stille in, *Comprehensive Organic Synthesis* (Eds., B.M. Trost, I. Fleming, M.F. Semmelhack), Pergamon Press, Oxford, 1991. (c) G. Consiglio in, *Catalytic Asymmetric Synthesis*, (Ed., I. Ojima), VCH, Weinheim, 1993. (d) G. Consiglio, P. Pino, *Top. Curr. Chem.*, 105 (1982) 77.
- [246] (a) BASF AG (W. Himmele, H. Siegel, W. Aquila, F.-J. Müller), DE 2 132 414 (1972); *Chem. Abstr.*, 78 (1973) 97.328. (b) C. Botteghi, C. Giambattista, P. Pino, *Chimia*, 26 (1972) 141. (c) M. Tanaka, Y. Watanabe, T. Mitsudo, K. Yamamoto, Y. Takegami, *Chem. Lett.* (1972), 483. (d) I. Ogata, Y. Ikeda, *Chem. Lett.* (1972), 487.
- [247] (a) N. Sakai, S. Mano, K. Nozaki, H. Takaya, *J. Am. Chem. Soc.*, 115 (1993) 7033. (b) N. Sakai, K. Nozaki, H. Takaya, *J. Chem. Soc., Chem. Commun.* (1994), 395. (c) T. Higashizima, N. Sakai, K. Nozaki, H. Takaya, *Tetrahedron Lett.*, 35 (1994) 2023.
- [248] Union Carbide (J.E. Babin, G.T. Whitecker), *PCT Int. Appl. WO 93/03839* (1993).
- [249] (a) Mitsubishi Gas Chem. Comp. and Takasago Int. Corp. (H. Takaya, N. Sakai, K.B.M. Tamao, S. Mano, H. Kumobayashi, T. Tomita), *Eur. Pat. EP 0.614 901* (1994); *Chem. Abstr.*, 122 (1994) 10.257. (b) Takasago Int. Corp. (K. Matsumura, T. Saito, N. Sayo, H. Kumobayashi, H. Takaya), *Eur. Pat. EP 0.614 902* (1994); *Chem. Abstr.*, 122 (1994) 31.704. (c) Takasago Int. Corp. (T. Saito, K. Matsumura, Y. Kato, N. Sayo, H. Kumobayashi), *Eur. Pat. EP 0.614 903* (1994).
- [250] C.G. Arena, F. Nicolo, D. Drommi, G. Bruno, F. Faraone, *J. Chem. Soc., Chem. Commun.* (1994), 2251.
- [251] (a) W. Reppe, *Experientia*, 5 (1949) 93. (b) W. Reppe, H. Vetter, *Liebigs Ann. Chem.*, 582 (1953) 133.
- [252] Texaco Dev. Co. (E.E. MacEntire, J.F. Knifton), *EP 0.240 193* (1986); *Chem. Abstr.*, 110 (1989) 134.785.
- [253] R.M. Laine, *J. Org. Chem.*, 45 (1980) 3370.
- [254] K. Murata, A. Matsuda, T. Matsuda, *J. Mol. Catal.*, 23 (1984) 121.
- [255] A.L. Lapidus, A.P. Rodin, L.Y. Brezhnev, I.G. Pruidze, B.I. Ugrak, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1990), 1448; *Chem. Abstr.*, 113: (1990) 171.812.
- [256] (a) T. Baig, P. Kalck, *J. Chem. Soc., Chem. Commun.* (1992), 1373. (b) T. Baig, J. Molinier, P. Kalck, *J. Organomet. Chem.*, 455 (1993) 219.
- [257] (a) J.F. Knifton, *Hydrocarbon Process.*, 60(12) (1981) 113. (b) J.F. Knifton, *CHEMTECH*, 11 (1981) 609.
- [258] L. Kaplan, *J. Org. Chem.*, 47 (1982) 5422.
- [259] (a) G. Jenner, *Applied Catal. A*, 121 (1995) 25. (b) G. Jenner, *J. Mol. Catal.*, 96 (1995) 215.
- [260] H. Kheradmand, A. Kiennemann, G. Jenner, *J. Organomet. Chem.*, 251 (1983) 339.
- [261] H. Bahrmann, B. Cornils, *Chem.-Ztg.*, 104 (1980) 39.
- [262] Recent references: (a) H. Knözinger, B.C. Gates, *Stud. Surf. Sci. Catal.*, 29 (1986) 531. (b) M. Ishino, M. Tamura, T. Deguchi, S. Nakamura, *J. Catal.*, 105 (1987) 478. (c) B.D. Dombek, *J. Organomet. Chem.*, 372 (1989) 151. (d) H. Ono, K. Fujiwara, M. Hashimoto, H. Watanabe, K. Yoshida, *J. Mol. Catal.*, 28 (1990) 289. (e) S. Nakamura, *CHEMTECH*, 20 (1990) 556. (f) M. Ishino, M. Tamura, T. Deguchi, S. Nakamura, *J. Catal.*, 133 (1992) 325.
- [263] Recent references: (a) K.G. Moloy, R.W. Wegman, *J. Chem. Soc., Chem. Commun.* (1988), 820. (b) G. Jenner, *J. Organomet. Chem.*, 346 (1988) 237. (c) K.G. Moloy, R.W. Wegman, *Organometallics*, 8 (1989) 2883. (d) M.J. Chen, J.W. Rathke, *Organometallics*, 8 (1989) 515. (e) N. Isogai, K. Tanaka, *J. Organomet. Chem.*, 397 (1990) 101. (f) E. Lindner, A. Bader, H. Braunling, R. Jira, *J. Mol. Catal.*, 57 (1990) 291. (g) N. Chatani, T. Sano, K. Ohe, Y. Kawasaki, S. Murai, *J. Org. Chem.*, 55 (1990) 5923. (h) G. Braca, A.M. Raspolli Galletti, G. Sbrana, E. Trabuco, *Adv. Chem. Ser.* 230 (1992) Chap. 21.
- [264] Recent references: (a) I. Matsuda, A. Ogiso, S. Sato, Y. Isumi, *J. Am. Chem. Soc.*, 111 (1989) 2332. (b) I. Matsuda, A. Ogiso, S. Sato, *J. Am. Chem. Soc.*, 112 (1990) 6120. (c) N. Chatani, S. Ikeda, K. Ohe, S. Murai, *J. Am. Chem. Soc.*, 114 (1992) 9710; (d) I. Ojima, P. Ingallina, R.J. Donovan, N. Clos, *Organometallics*, 10 (1991) 38. (e) I. Ojima, M. Tzamarioudaki, C.Y. Tsai, *J. Am. Chem. Soc.*, 116 (1994) 3643. (f) F. Monteil, I. Matsuda, H. Alper, *J. Am. Chem. Soc.*, 117 (1995) 4419 and references cited therein.
- [265] Union Carbide Corp. (R.L. Pruet, J.A. Smith), *US 3,527,809* (1967).
- [266] Anonymous, *Chem. Eng.*, 84 (1977) 110.
- [267] E.A.V. Brewster, *Chem. Eng.*, 83 (1976), 90.
- [268] Johnson, Matthey and Co., (G. Wilkinson), *DE-AS 1,939,322* (1969).
- [269] Union Carbide Corp., (R.L. Pruet, J.A. Smith), *US 3,527,809* (1967).
- [270] Union Carbide Corp., (R.L. Pruet, J.A. Smith), *US 4,148,830* (1969).
- [271] Union Carbide Corp., (R.L. Pruet, J.A. Smith), *DE-OS 2,062,703* (1971).
- [272] Union Carbide Corp., (D.G. Morrell, P.D. Sherman), *DE-OS 2,802,922* (1978).
- [273] Union Carbide Corp., (W. Otte et al.), *EP 0.017,183* (1980).
- [274] Union Carbide Corp., (E.A.V. Brewster, R.L. Pruet), *DE-PS 2,715,685* (1977).
- [275] Union Carbide Corp., (D.L. Bunning, D.B. Stanton), *EP 0.097,891* (1983).
- [276] Davy Powergas Ltd., (R. Fowler), *GB 1,387,657* (1973).
- [277] Union Carbide Corp., (D.L. Bunning, M.A. Blessing), *EP 0.188,246* (1986).

- [278] Union Carbide Corp., (K.D. Sorensen), EP 0.484,976 (1991).
- [279] Union Carbide Corp., (D.L. Bunning), EP 0.404,193 (1990).
- [280] Union Carbide Corp., (E.A.V. Brewester, R.L. Pruett), DE-PS 2,715,686 (1977).
- [281] BASF AG, (R. Kummer, K. Schwirten), DE-OS 3,301,591 (1983).
- [282] BASF AG, (R. Zehner et al.), DE-OS 3,625,261 (1986).
- [283] BASF AG, (K. Fischer et al.), DE-OS 3,114,147 (1981).
- [284] BASF AG, (P. Zehner et al.), EP 0.254,180 (1987).
- [285] Celanese Corp. Business Report (1974), p.9.
- [286] Davy International (Oil and Chemicals) Ltd., LP Oxo Process, Evaluation Data (1979).
- [287] Mitsubishi Kasei Corp., (T. Mori, A. Ueda, K. Fujita), DE-OS 4,419,898 (1994).
- [288] Exxon Chem., (J.A. Hanin), EP 0.343,819 (1989).
- [289] Exxon Res.Eng., (J.A. Hanin), EP 0.183,545 (1985).
- [290] a) H.M. Colquhoun, D.J. Thompson, M.V. Twigg, Carbonylation, Direct Synthesis of Carbonyl Compounds, Plenum Press, New York, 1991; b) G.W. Parshall, S.D. Ittel, Homogeneous Catalysis, Wiley, New York, 1992; c) A. Mortreux, F. Petit, Industrial Applications of Homogeneous Catalysis, Reidel, Dordrecht, 1988; d) R.F. Heck, Palladium Reagents in Organic Syntheses, Academic Press, 1985; e) G.P. Chiusoli, *Trans. Met. Chem.*, 16 (1991) 553; f) F.J. Waller, *J. Mol. Catal.*, 31 (1985) 123; g) M. Röper, *Stud. Surf. Sci. Catal.*, 64 (1991) 381; h) W. Keim, *J. Organomet. Chem.*, 372 (1989) 15; i) W. Bertleff, in, *Ullmann's Encyclopedia of Industrial Chemistry*, 5th Ed., Vol. A5, Verlag Chemie Weinheim, (1986), 217; j) M.M. Taqui Khan, *Platinum Met. Rev.*, 35 (1991) 70.
- [291] (a) T. Chenal, I. Cipres, J. Jenck, P. Kalck, Y. Peres, *J. Mol. Catal.*, 78 (1993) 351; b) L. Garlaschelli, M. Marchionna, M.C. Iapalucci, G. Longoni, *J. Organomet. Chem.*, 378 (1989) 457; c) M. Miekuz, F. Joo, H. Alper, *Organometallics*, 6 (1987) 1591; d) G. Cavinato, L. Toniolo, C. Botteghi, *J. Mol. Catal.*, 32 (1985) 211; e) H. Alper, J.B. Woell, B. Despeyroux, D.J.H. Smith, *J. Chem. Soc., Chem. Commun.*, (1983) 1270; f) G. Consiglio, L. Kollar, R. Kolliker, *J. Organomet. Chem.*, 396 (1990) 375.
- [292] C.W. Lee, H. Alper, *J. Org. Chem.*, 60 (1995) 250.
- [293] (a) B. El Ali, H. Alper, *J. Org. Chem.*, 58 (1993) 3595; b) B. El Ali, H. Alper, *J. Mol. Catal.*, 77 (1992) 7.
- [294] (a) B. El Ali, H. Alper, *J. Mol. Catal.*, 80 (1993) 377; b) B. El Ali, G. Vasapollo, H. Alper, *J. Org. Chem.*, 58 (1993) 4739.
- [295] G. Consiglio, S.C.A. Nefkens, C. Pisano, F. Wenzinger, *Helv. Chim. Acta*, 74 (1991) 323.
- [296] I.J.B. Lin, H. Alper, *J. Chem. Soc., Chem. Commun.*, (1989) 248.
- [297] D.D.M. Wayner, F.W. Hartstock, *J. Mol. Catal.*, 48 (1988) 15.
- [298] M. Hidai, Y. Koyasu, K. Chikanari, Y. Uchida, *J. Mol. Catal.*, 40 (1987) 243.
- [299] A. Behr, U. Kanne, W. Keim, *J. Mol. Catal.*, 35 (1986) 19.
- [300] J.F. Knifton, *J. Catal.*, 60 (1979) 27.
- [301] Idemitsu Petrochem. Co. (M. Kanzawa, T. Ishibashi, T. Kumazawa), JP 03.255.054 (1991); *Chem. Abstr.*, 116 (1992) 151164w.
- [302] G. Vasapollo, A. Somasunderam, B. El Ali, H. Alper, *Tetrahedron Lett.*, 34 (1994) 6203.
- [303] C. Botteghi, G.D. Ponte, M. Marchetti, S. Paganelli, *J. Mol. Catal.*, 93 (1994) 1.
- [304] (a) R. Takeuchi, N. Ishii, M. Sugiura, N. Sato, *J. Org. Chem.*, 57 (1992) 4189; (b) M.M. Doyle, W.R. Jackson, P. Perlmutter, *Tetrahedron Lett.*, 30 (1989) 233.
- [305] G.M. Wieber, L.S. Hegedus, B. Akermark, E.T. Michalson, *J. Org. Chem.*, 54 (1989) 4649.
- [306] (a) G. Chelucci, M.A. Cabras, C. Botteghi, M. Marchetti, *Tetrahedron Asymm.*, 5 (1994) 299; b) G. Consiglio, L. Roncetti, *Chirality*, 3 (1991) 341; c) T. Hiyama, N. Wakasa, T. Kusumoto, *Synlett*, (1991) 569.
- [307] H. Alper, N. Hamel, *J. Am. Chem. Soc.*, 112 (1990) 2803.
- [308] H. Alper, N. Hamel, *J. Chem. Soc., Chem. Commun.*, (1990) 1356.
- [309] A. Sisak, F. Ungvary, L. Marko, *J. Org. Chem.*, 55 (1990) 2508.
- [310] (a) Review: A. Sen, *Adv. Polym. Sci.*, 73/74 (1986) 125; b) E. Drent, *Pure Appl. Chem.*, 62 (1990) 661; c) A. Sen, T.-W. Lai, *J. Am. Chem. Soc.*, 104 (1982) 3520; d) A. Sen, T.-W. Lai, *Organometallics*, 3 (1984) 866; e) U. Klabunde, S.D. Ittel, *J. Mol. Catal.*, 41 (1987) 123; f) Shell (E. Drent), EP 0.121.965 (1984); *Chem. Abstr.*, 102: 46423 (1985); g) Shell (E. Drent), EP 0.399.617 (1990); *Chem. Abstr.*, 114: 165108 (1991); h) M. Yoneyama, M. Kakimoto, Y. Imai, *Macromolecules*, 22 (1989) 2593.
- [311] (a) G. Consiglio, B. Studer, F. Oldani, P. Pino, *J. Mol. Catal.*, 58 (1990) L9; b) S.J. Tremont, E.E. Remsen, P.L. Mills, *Macromolecules*, 23 (1990) (1984).
- [312] E. Drent, J.A.M. van Broekhoven, M.J. Doyle, *J. Organomet. Chem.*, 417 (1991) 235.
- [313] A. Batistini, G. Consiglio, *Organometallics*, 11 (1992) 1766.
- [314] M. Brookhart, F.C. Rix, J.M. DeSimone, J.C. Barborak, *J. Am. Chem. Soc.*, 114 (1992) 5894.
- [315] Anonymous, *European Chem. News*, Jan. 23 (1995) 36.
- [316] P. Brechot, Y. Chauvin, D. Commereux, L. Saussine, *Organometallics*, 9 (1990), 26.
- [317] A.R. El Man, O.V. Boldyreva, E.V. Slivinskii, S.M. Loktev, *Izv. Akad. Nauk, Ser. Khim.*, 3 (1992) 552.
- [318] Shell AG (E. Drent), EP 00.231.044 (1986); *Chcm. Abstr.*, 108: (1988) 166.984.
- [319] G.E. Morris, D. Oakley, D.A. Pippard, D.J.H. Smith, *J. Chem. Soc., Chem. Commun.*, (1987) 410.
- [320] S.C.A. Nefkens, M. Sperrle, G. Consiglio, *Angew. Chem.*, 105 (1993) 1837.

- [321] M.F. Semmelhack, C. Kim, N. Zhang, C. Bodurow, M. Sanner, W. Dobler, M. Meier, *Pure Appl. Chem.*, 62 (1990) 2035.
- [322] (a) Y. Tamaru, M. Hojo, Z. Yoshida, *Tetrahedron Lett.*, 28 (1987) 325; b) S. Toda, M. Miyamoto, H. Kinoshita, K. Inomata, *Bull. Chem. Soc. Jpn.*, 64 (1991) 3600.
- [323] M.F. Semmelhack, C. Bodurow, *J. Am. Chem. Soc.*, 106 (1984) 1496.
- [324] J.S. Yadav, E.S. Rao, V.S. Rao, B.M. Choudary, *J. Mol. Catal.*, 49 (1989) L61.
- [325] I. Amer, H. Alper, *J. Organomet. Chem.*, 383 (1990) 573.
- [326] (a) Y. Kushino, K. Itoh, M. Miura, M. Nomura, *J. Mol. Catal.*, 89 (1994) 151; b) D. Zargarian, H. Alper, *Organometallics*, 12 (1993) 712; c) K. Itoh, M. Miura, M. Nomura, *Tetrahedron Lett.*, 33 (1992) 5369; d) B.E. Ali, H. Alper, *J. Mol. Catal.*, 67 (1991) 29.
- [327] S. Torri, H. Okumoto, M. Sadakane, L.H. Xu, *Chem. Lett.*, (1991) 1673.
- [328] O. Ouerfelli, M. Ishida, H. Shinozaki, K. Nakanishi, Y. Ohfuné, *Synlett*, (1993) 409.
- [329] E. Drent, P. Arnoldy, P.H.M. Budzelaar, *J. Organomet. Chem.*, 455 (1993) 247.
- [330] J.T. Lee, H. Alper, *Tetrahedron Lett.*, 32 (1991) 1769.
- [331] (a) D. Zargarian, H. Alper, *Organometallics*, 10 (1991) 2914; b) Y. Tamaru, M. Hojo, Z. Yoshida, *J. Org. Chem.*, 56 (1991) 1099; c) H. Alper, B. Despeyroux, J.B. Woell, *Tetrahedron Lett.*, 24 (1983) 5691.
- [332] F.W. Hartstock, L.B. McMahon, I.P. Tell, *Tetrahedron Lett.*, 34 (1993) 8067.
- [333] (a) B. Gabriele, M. Costa, G. Salerno, G.P. Chiusoli, *J. Chem. Soc., Chem. Commun.*, (1994) 1429; b) B. Gabriele, M. Costa, G. Salerno, G.P. Chiusoli, *J. Chem. Soc., Perkin Trans. 1*, (1994) 83; c) B. Gabriele, M. Costa, G. Salerno, G.P. Chiusoli, *J. Chem. Soc., Chem. Commun.*, (1992) 1007.
- [334] (a) N.E. Schore in B.M. Trost (Ed.), *Comprehensive Organic Synthesis*, Vol. 5, Pergamon, Oxford (1991), p. 1037; b) N.E. Schore, *Chem. Rev.*, 88 (1988) 1081.
- [335] (a) D.C. Billington, *Tetrahedron Lett.*, 24 (1983) 2905; b) P. Magnus, L.M. Principe, M.J. Slater, *J. Org. Chem.*, 52 (1987) 1483; c) D.C. Billington, W.J. Kerr, P.L. Pauson, C.F. Farnochi, *J. Organomet. Chem.*, 356 (1988) 213; S.E. MacWhorter, V. Sampath, M.M. Olmstead, N.E. Schore, *J. Org. Chem.*, 53 (1988) 203.
- [336] G.P. Chiusoli, M. Costa, M. Gerbella, G. Salerno, *Gazz. Chim. Ital.*, 115 (1985) 697.
- [337] (a) T. Joh, H. Nagata, S. Takahashi, *Inorg. Chim. Acta*, 220 (1994) 45; b) T. Joh, H. Nagata, S. Takahashi, *Chem. Lett.*, (1992) 1305; c) T. Joh, K. Doyama, K. Onitsuka, T. Shiohara, S. Takahashi, *Organometallics*, 10 (1991) 2493; d) K. Doyama, T. Joh, K. Onitsuka, T. Shiobara, S. Takahashi, *J. Chem. Soc., Chem. Commun.*, (1987) 649.
- [338] V. Rautenstrauch, P. Megrard, J. Conesa, W. Kuster, *Angew. Chem. Int. Ed. Engl.*, 29 (1990) 1413.
- [339] N. Jeong, S.H. Hwang, Y. Lee, Y.K. Chung, *J. Am. Chem. Soc.*, 116 (1994) 3159.
- [340] (a) P. Hong, T. Mise, H. Yamazaki, *J. Organomet. Chem.*, 412 (1991) 291; b) T. Mise, P. Hong, H. Yamazaki, *J. Org. Chem.*, 48 (1983) 238; c) P. Hong, T. Mise, H. Yamazaki, *Chem. Lett.*, (1981) 989.
- [341] P. Hong, T. Mise, H. Yamazaki, *J. Organomet. Chem.*, 334 (1987) 129.
- [342] K.-T. Huh, A. Orita, H. Alper, *J. Org. Chem.*, 58 (1993) 6956.
- [343] (a) N. Satyanarayana, H. Alper, *Organometallics*, 10 (1991) 804; (b) K. Matsushita, T. Komori, S. Oi, Y. Inoue, *Tetrahedron Lett.*, 35 (1994) 5889; (c) H. Arzoumanian, F. Cochini, D. Nuel, N. Rosas, *Organometallics*, 12 (1993) (1871); (d) J. Tsuji, T. Sugiura, I. Minami, *Tetrahedron Lett.*, 27 (1986) 731; (e) N.D. Trieu, C.J. Elsevier, K. Vrieze, *J. Organomet. Chem.*, 325 (1987) C23; f) J. Kiji, H. Konishi, T. Okano, S. Kometani, A. Iwasa, *Chem. Lett.*, (1987) 313; g) T. Mandai, Y. Tsujiguchi, S. Matsuoka, J. Tsuji, S. Saito, *Tetrahedron Lett.*, 35 (1994) 5697; h) Y. Tsuji, T. Kondo, Y. Watanabe, *J. Mol. Catal.*, 40 (1987) 295.
- [344] S. Murai, N. Chatani, Y. Fukumoto, T. Ida, *J. Am. Chem. Soc.*, 115 (1993) 11 614.
- [345] R. Takeuchi, H. Yasue, *J. Org. Chem.*, 58 (1993) 5386.
- [346] Y.V. Gulevich, N.A. Bumagin, I.P. Beletskaya, *Russ. Chem. Rev.*, 57 (1988) 299.
- [347] (a) P. Timmermann, W. Verboom, D.N. Reinhoudt, A. Arduini, S. Grandi, A.R. Sicuri, A. Pochini, R. Ungaro, *Synthesis*, (1994) 185; b) V.A. Burgess, S.G. Davies, R.T. Skerlj, M. Whittaker, *Tetrahedron Asymm.*, 3 (1992) 871; c) A.D. Rama, D.S. Iyengar, M. Pardhasaradhi, *Tetrahedron*, 50 (1994) 2543; d) A.D. Rama, D.S. Iyengar, M. Pardhasaradhi, *Synth. Commun.*, 23 (1993) 509; e) M.G. Bamwell, J.R. Dupuche, *Aust. J. Chem.*, 47 (1994) 203; f) T. Hiyama, N. Wakasa, T. Ueda, T. Kusumoto, *Bull. Chem. Soc. Jpn.*, 63 (1990) 640.
- [348] (a) I. Amer, H. Alper, *J. Org. Chem.*, 53 (1988) 5147; b) H. Alper, I. Amer, G. Vasapollo, *Tetrahedron Lett.*, 30 (1989) 2615.
- [349] (a) K. Kikukawa, K. Kono, K. Nagira, F. Wada, T. Matsuda, *J. Org. Chem.*, 46 (1981) 4413; b) K. Kikukawa, T. Totoki, F. Wada, T. Matsuda, *J. Organomet. Chem.*, 270 (1984) 283.
- [350] a) Review: K. Ritter, *Synthesis*, (1993) 735; b) U. Gerlach, T. Wollmann, *Tetrahedron Lett.*, 33 (1992) 5499; c) S. Cacchi, A. Lupi, *Tetrahedron Lett.*, 33 (1992) 3939; d) G.T. Crisp, A.G. Meyer, *J. Org. Chem.*, 57 (1992) 6972; d) J. Wrobel, A. Dietrich, *Tetrahedron Lett.*, 34 (1993) 3543; e) Y. Uozumi, N. Suzuki, A. Ogiwara, T. Hayashi, *Tetrahedron*, 50 (1994) 4293; f) M. Ishikura, M. Terashima, *J. Org. Chem.*, 59 (1994) 2634; g) C. Haffner, *Tetrahedron Lett.*, 35 (1994) 1349.
- [351] G. Cometti, A. Du Vosel, F. Francalanci, R. Santi, W. Cabri, M. Foa, *J. Organomet. Chem.*, 451 (1993) C13.
- [352] G.P. Roth, J.A. Thomas, *Tetrahedron Lett.*, 33 (1992) (1959).
- [353] V.V. Grushin, H. Alper, *J. Org. Chem.*, 58 (1993) 4794.

- [354] (a) N.A. Bumagin, K.V. Nikitin, I.P. Beletskaya, *J. Organomet. Chem.*, 358 (1988) 563; b) D. Valentine, J.W. Tilley, R.A. Le Mahien, *J. Org. Chem.*, 46 (1981) 4614; c) J.T. Lee, H. Alper, *Organometallics*, 9 (1990) 3064.
- [355] M. Foa, F. Francalani, A. Gardano, G. Cainelli, A. Umani-Ronchi, *J. Organomet. Chem.*, 248 (1983) 225.
- [356] a) R.A. Head, A. Ibbotson, *Tetrahedron Lett.*, 25 (1984) 5939; b) D.E. Bergbreiter, B. Chen, D. Weatherford, *J. Mol. Catal.*, 74 (1992) 409; c) K.V. Nikitin, N.P. Andryukhova, N.A. Bumagin, I.P. Beletskaya, *Mendeleev Commun.*, 4 (1991) 129; d) R. Vanderesse, J. Marchal, P. Caubere, *Synth. Commun.*, 23 (1993) 1361; e) K. Maeda, H. Yagita, K. Omata, K. Fujimoto, *J. Mol. Catal.*, 71 (1992) 347.
- [357] T. Kobayashi, M. Tanaka, *J. Organomet. Chem.*, 233 (1982) C64.
- [358] (a) T. Sakakura, M. Claisupakitsin, T. Hayashi, M. Tanaka, *J. Organomet. Chem.*, 334 (1987) 205; b) T. Okano, N. Harada, J. Kiji, *Bull. Chem. Soc. Jpn.*, 65 (1992) 1741.
- [359] (a) R.J. Perry, B.D. Wilson, R.J. Miller, *J. Org. Chem.*, 57 (1992) 2883; b) R.J. Perry, B.D. Wilson, *J. Org. Chem.*, 57 (1992) 6351.
- [360] R.J. Perry, B.D. Wilson, *Organometallics*, 13 (1994) 3346.
- [361] I. Pri-Bar, H. Alper, *J. Org. Chem.*, 54 (1989) 36.
- [362] R.J. Perry, S.R. Turner, *J. Org. Chem.*, 56 (1991) 6573.
- [363] (a) W.R. Moser, A.W. Wang, N.K. Kildahl, *J. Am. Chem. Soc.*, 110 (1988) 2816; b) W.R. Moser, A.W. Wang, N.K. Kildahl, *Chem. Ind. (Dekker)*, 40 (1990) 137.
- [364] (a) J.-J. Brunet, C. Sidot, P. Caubere, *Tetrahedron Lett.*, 22 (1981) 1013; b) T. Kashimura, K. Kudo, S. Mori, N. Sugita, *Chem. Lett.*, (1986) 299; c) K. Kudo, T. Shibata, T. Kashimura, S. Mori, N. Sugita, *Chem. Lett.*, (1987) 577.
- [365] (a) M. Foa, F. Francalanci, *J. Mol. Catal.*, 41 (1987) 89; b) F. Francalanci, E. Bencini, A. Gardano, M. Vincenti, M. Foa, *J. Organomet. Chem.*, 301 (1986) C27; c) M. Foa, F. Francalanci, E. Bencini, A. Gardano, *J. Organomet. Chem.*, 285 (1985) 293; d) M. Miura, K. Itoh, M. Nomura, *J. Mol. Catal.*, 48 (1988) 11.
- [366] (a) X. Huang, J.L. Wu, *Chem. Ind.*, (1990) 548; b) F. Monteil, P. Kalck, *J. Organomet. Chem.*, 482 (1994) 45.
- [367] K. Maeda, H. Yagita, K. Omata, K. Fujimoto, *J. Mol. Catal.*, 71 (1992) 347.
- [368] B.M. Choudary, N.P. Reddy, B. Ashok, *Appl. Catal.*, 32 (1987) 357.
- [369] (a) M. Yoneyama, M. Kakimoto, Y. Imai, *Macromolecules*, 22 (1989) 2593; b) R.J. Perry, S.R. Turner, R.W. Blevins, *Macromolecules*, 26 (1993) 1509; c) Y. Kubota, K. Takeuchi, T. Hanaoka, Y. Sugi, *Bull. Chem. Soc. Jpn.*, 67 (1994) 563.
- [370] (a) Y. Kubota, T. Hanaoka, K. Takeuchi, Y. Sugi, *Synlett*, (1994) 515; (b) Y. Kubota, T. Hanaoka, K. Takeuchi, Y. Sugi, *J. Chem. Soc., Chem. Commun.*, (1994) 1553.
- [371] (a) H. Alper, S. Antebi, J.B. Woell, *Angew. Chem. Int. Ed. Engl.*, 23 (1984) 732; *Angew. Chem.*, 96 (1984) 710; b) J.B. Woell, S.B. Fergusson, H. Alper, *J. Org. Chem.*, 50 (1985) 2134; c) K.E. Hashem, J.B. Woell, H. Alper, *Tetrahedron Lett.*, 25 (1984) 4879.
- [372] N.A. Bumagin, Y.V. Gulevich, I.P. Beletskaya, *J. Organomet. Chem.*, 285 (1985) 415.
- [373] H. Watanabe, Y. Hashizume, K. Uneyama, *Tetrahedron Lett.*, 33 (1992) 4333.
- [374] Y. Ben-David, M. Portnoy, D. Milstein, *J. Am. Chem. Soc.*, 111 (1989) 8742.
- [375] M. Huser, M.T. Youinou, J.A. Osborn, *Angew. Chem.*, 101 (1989) 1427.
- [376] V.V. Grushin, H. Alper, *J. Chem. Soc., Chem. Commun.*, (1992) 611.
- [377] T. Kashimura, K. Kudo, S. Mori, N. Sugita, *Chem. Lett.*, (1986) 851.
- [378] R. Mutin, C. Lucas, J. Thivolle-Cazat, V. Dufaud, F. Dany, J.M. Basset, *J. Chem. Soc., Chem. Commun.*, (1988) 896.
- [379] V. Dufaud, J. Thivolle-Cazat, J.M. Basset, *J. Chem. Soc., Chem. Commun.*, (1990) 426.
- [380] (a) R. Takeuchi, K. Suzuki, N. Sato, *Synthesis*, (1990) 923; b) R. Takeuchi, K. Suzuki, N. Sato, *J. Mol. Catal.*, 66 (1991) 277.
- [381] (a) T. Kobayashi, M. Tanaka, *J. Organomet. Chem.*, 233 (1982) C64; b) F. Ozawa, H. Soyama, T. Yamamoto, A. Yamamoto, *Tetrahedron Lett.*, 23 (1982) 3383; c) F. Ozawa, H. Soyama, H. Yanagihara, I. Aoyama, H. Takino, K. Izawa, T. Yamamoto, A. Yamamoto, *J. Am. Chem. Soc.*, 107 (1985) 3235; d) J. Collin, *Bull. Soc. Chim. Fr.*, (1988) 976.
- [382] (a) F. Ozawa, N. Kawasaki, H. Okamoto, T. Yamamoto, A. Yamamoto, *Organometallics*, 6 (1987) 1640; b) M. Tanaka, T. Kobayashi, T. Sakakura, H. Itatani, S. Danno, K. Zushi, *J. Mol. Catal.*, 32 (1985) 115; c) H. Yamashita, T. Sakakura, T. Kobayashi, M. Tanaka, *J. Mol. Catal.*, 48 (1988) 69; d) T. Sakakura, H. Yamashita, T. Kobayashi, T. Hayashi, M. Tanaka, *J. Org. Chem.*, 52 (1987) 5733; e) L. Huang, F. Ozawa, A. Yamamoto, *Organometallics*, 9 (1990) 2603.
- [383] (a) T. Okano, N. Harada, J. Kiji, *Bull. Chem. Soc. Jpn.*, 67 (1994) 2329; b) Y. Misumi, Y. Ishii, M. Hidai, *J. Mol. Catal.*, 78 (1993) 1; c) Y. Ben-David, M. Portnoy, D. Milstein, *J. Chem. Soc., Chem. Commun.*, (1989) 1816; d) I. Pri-Bar, O. Buchman, *J. Org. Chem.*, 49 (1984) 4009; e) V.P. Baillargeon, J.K. Stille, *J. Am. Chem. Soc.*, 108 (1986) 452; f) V.P. Baillargeon, J.K. Stille, *J. Am. Chem. Soc.*, 105 (1983) 7175.
- [384] (a) M. Ishikura, M. Terashima, *J. Org. Chem.*, 59 (1994) 2634; b) J.J. Brunet, M. Taillefer, *J. Organomet. Chem.*, 384 (1990) 190; c) A.M. Echavarren, J.K. Stille, *J. Am. Chem. Soc.*, 110 (1988) 1557; d) A.C. Gyorkos, J.K. Stille, S.L. Hegedus, *J. Am. Chem. Soc.*, 112 (1990) 8465; e) Y. Hatanaka, S. Fukushima, T. Hiyama, *Tetrahedron*, 48 (1992) 2113; f) T. Ohe, K. Ohe, S. Uemura, N. Sugita, *J. Organomet. Chem.*, 344 (1988) C5; g) T. Kondo, Y. Tsuji, Y. Watanabe, *J. Organomet. Chem.*, 345 (1988) 397; h) H. Yamashita, T. Kobayashi, T. Sakakura, M. Tanaka, *J. Organomet. Chem.*, 356 (1988) 125; i) T. Sakamoto, A. Yasuhara, Y. Kondo, H. Yamanaka, *Chem. Pharm. Bull.*, 40 (1992) 1137; k) R. Grigg, J. Redpath, V. Sridharan, D. Wilson, *Tetrahedron Lett.*, 35 (1994) 4429.
- [385] M. Tanaka, *Bull. Chem. Soc. Jpn.*, 54 (1981) 637.

- [386] (a) L. Delaude, A.M. Masdeu, H. Alper, *Synthesis*, (1994) 1149; b) S. Torii, H. Okumoto, L.H. Xu, M. Sadakane, M.V. Shostakovskiy, A.B. Ponomaryov, V.N. Kalinin, *Tetrahedron*, 49 (1993) 6773; c) S. Torii, L.H. Xu, H. Okumoto, *Synlett*, (1991) 695; d) T. Kobayashi, M. Tanaka, *J. Chem. Soc., Chem. Commun.*, (1981) 333.
- [387] K. Nozaki, N. Sato, H. Takaya, *J. Org. Chem.*, 59 (1994) 2679.
- [388] Y. Misumi, Y. Ishii, M. Hidai, *Chem. Lett.*, (1994) 695.
- [389] (a) S.D. Knight, L.E. Overman, G. Pairaudeau, *J. Am. Chem. Soc.*, 115 (1993) 9293; b) E.I. Negishi, Y. Zhang, I. Shimoyama, G. Wu, *Tetrahedron Lett.*, 31 (1990) 2841; c) S. Torii, H. Okumoto, L.H. Xu, *Tetrahedron Lett.*, 31 (1990) 7175; d) W. Tilley, D.L. Coffen, B.H. Schaer, J. Lind, *J. Org. Chem.*, 52 (1987) 2469.
- [390] E.-I. Negishi, Y. Zhang, I. Shimoyama, G. Wu, *J. Am. Chem. Soc.*, 111 (1989) 8018.
- [391] B. Morin-Phelippeau, A. Favre-Fatet, F. Hugues, D. Commereuc, Y. Chauvin, *J. Mol. Catal.*, 51 (1989) 145.
- [392] H. Alper, G. Vasopolo, *Tetrahedron Lett.*, 30 (1989) 2617.
- [393] S.-I. Murahashi, Y. Mitsue, K. Ike, *J. Chem. Soc., Chem. Commun.*, (1987) 125.
- [394] N. Kalinin, M.V. Shostakovskiy, A.B. Ponomaryov, *Tetrahedron Lett.*, 31 (1990) 4073.
- [395] (a) Z. An, M. Catallani, G.P. Chiusoli, *J. Organomet. Chem.*, 371 (1989) C51; (b) Z. An, M. Catallani, G.P. Chiusoli, *Gazz. Chim. Ital.*, 120 (1990) 383.
- [396] Z. An, M. Catallani, G.P. Chiusoli, *J. Organomet. Chem.*, 397 (1990) C31.
- [397] (a) K. Okuro, M. Furune, M. Miura, M. Nomura, *J. Org. Chem.*, 57 (1992) 4754; (b) Y. Inoue, M. Taniguchi, H. Hashimoto, K. Ohuchi, S. Imaizumi, *Chem. Lett.*, (1988) 81.
- [398] A. Arcadi, S. Cacchi, V. Carnicelli, F. Marinelli, *Tetrahedron*, 50 (1994) 437.
- [399] (a) T. Sugihara, C. Coperet, Z. Owczarczyk, L.S. Harring, E.-I. Negishi, *J. Am. Chem. Soc.*, 116 (1994) 7923; b) R. Grigg, P. Kennewell, A.J. Teasdale, *Tetrahedron Lett.*, 33 (1994) 7789; E.-I. Negishi, *Pure Appl. Chem.*, 64 (1992) 323; c) R. Grigg, H. Khalil, P. Levett, J. Virica, V. Sridharan, *Tetrahedron Lett.*, 35 (1994) 3197.
- [400] (a) C.S. Cho, K. Tanabe, O. Itoh, S. Uemura, *J. Org. Chem.*, 60 (1995) 274; (b) N. Miyaura, A. Suzuki, *Chem. Lett.*, (1981) 879; b) S. Uemura, H. Takahashi, K. Ohe, N. Sugita, *J. Organomet. Chem.*, 361 (1989) 63; c) K. Ohe, H. Takahashi, S. Uemura, N. Sugita, *J. Org. Chem.*, 52 (1987) 4859; d) R.C. Larock, C.A. Fellows, *J. Am. Chem. Soc.*, 104 (1982) (1900).
- [401] D. Forster, T.C. Singleton, *J. Mol. Catal.*, 17 (1982) 299.
- [402] Hoechst AG (H. Erpenbach, K. Gehrmann, H.K. Kübbeler), EP 0.008.396; *Chem. Abstr.*, 93: (1980) 45.992 m; Hoechst AG (H. Erpenbach, K. Gehrmann, W. Lork, P. Prinz), EP 0.048.335; *Chem. Abstr.*, 97: 109.563q.
- [403] (a) V.H. Agreda, L.R. Partin, W.H. Heise, *Chem. Eng. Prog.*, (1990) 40; b) J. Haggin, *Chem. Eng. News*, 68 (1990) 30; c) Eastman Chem. Co. (C. Hewlett), US 4.559.183 (1985).
- [404] J.N. Armor, *Appl. Catal.*, 78 (1991) 141.
- [405] (a) C.E. Hickey, P.M. Maitlis, *J. Chem. Soc., Chem. Commun.*, (1984) 1609; (b) G. Luft, M. Schrod, *J. Mol. Catal.*, 20 (1983) 175; c) M. Schrod, G. Luft, J. Grobe, *J. Mol. Catal.*, 22 (1983) 169.
- [406] Eastman Kodak Co. (T.H. Larkins, S.W. Polichnowski, G.C. Tustin, D.A. Young), US Patent 04.374.070 (1983).
- [407] T.W. Dekleva, D. Forster, *J. Am. Chem. Soc.*, 107 (1985) 3565.
- [408] H. Urata, H. Maekawa, S. Takahashi, T. Fuchikami, *J. Org. Chem.*, 56 (1991) 4320.
- [409] H. Yagita, H. Kuwahara, K. Omata, K. Fujimoto, *Chem. Lett.*, (1990) 335.
- [410] M. Urata, H. Yugari, T. Fuchikami, *Chem. Lett.*, (1987) 833.
- [411] H. Urata, D. Goto, T. Fuchikami, *Tetrahedron Lett.*, 32 (1991) 3091.
- [412] H. Alper, N. Hamel, *Tetrahedron Lett.*, 28 (1987) 3237.
- [413] D. Roberto, H. Alper, *J. Am. Chem. Soc.*, 111 (1989) 7539.
- [414] H. Alper, H. Arzoumanian, J.F. Petrigani, M. Saldana-Maldonado, *J. Chem. Soc., Chem. Commun.*, (1985) 340.
- [415] S. Calet, H. Alper, J.F. Petrigani, H. Arzoumanian, *Organometallics*, 6 (1987) 1625.
- [416] (a) Shell (E. Drent), EP 0.577.206 (1993); b) Shell (E. Drent, E. Kragtwijk), US 5.359.081 (1994).
- [417] (a) S. Calet, F. Urso, H. Alper, *J. Am. Chem. Soc.*, 111 (1989) 931; b) H. Alper, *Pure Appl. Chem.*, 60 (1988) 35.
- [418] (a) I. Amer, H. Alper, *J. Am. Chem. Soc.*, 111 (1989) 927; b) F. Joo, H. Alper, *Organometallics*, 4 (1985) 1775; c) S.R. Adapa, C.S.N. Prasad, *J. Chem. Soc., Perkin Trans. I*, (1989) 1706.
- [419] (a) Y. Hu, J.-X. Wang, W. Cui, *Synth. Commun.*, 24 (1994) 1743; b) S.C. Shim, C.H. Doh, W.H. Park, Y.G. Kwon, H.S. Lee, *J. Organomet. Chem.*, 382 (1990) 419; c) J.J. Brunet, C. Sidot, P. Caubere, *J. Org. Chem.*, 48 (1983) (1919); d) T. Imamoto, T. Kusumoto, M. Yokoyama, *Bull. Chem. Soc. Jpn.*, 55 (1982) 643; e) M. Foa, F. Francalanci, E. Bencini, A. Gardano, *J. Organomet. Chem.*, 285 (1985) 293; f) V. Galamb, G. Palyi, F. Ungvary, L. Marko, R. Boese, G. Schmid, *J. Am. Chem. Soc.*, 108 (1986) 3344.
- [420] S.-I. Murahashi, Y. Imada, *Chem. Lett.*, (1985) 1477.
- [421] J.F. Knifton, *J. Organomet. Chem.*, 188 (1980) 220.
- [422] (a) G. Tanguy, B. Weinberger, H. Des Abbayes, *Tetrahedron Lett.*, 24 (1983) 4005; b) S.G. Davies, A.J. Smallridge, A. Ibbotson, *J. Organomet. Chem.*, 386 (1990) 195.

- [423] (a) T. Okano, N. Okabe, J. Kiji, *Bull. Chem. Soc. Jpn.*, 65 (1992) 2589; b) H. Alper, K. Hashem, J. Heveling, *Organometallics*, 1 (1982) 775; c) S.R. Adapa, C.S.N. Prasad, *J. Chem. Soc. Perkin Trans. 1*, (1989) 1706; d) K. Yamamoto, R. Deguchi, J. Tsuji, *Bull. Chem. Soc. Jpn.*, 58 (1985) 3397; e) T. Takahashi, H. Ikeda, J. Tsuji, *Tetrahedron Lett.*, 21 (1980) 3885; f) T. Kobayashi, M. Tanaka, *J. Mol. Catal.*, 47 (1988) 41; g) T. Kobayashi, F. Abe, M. Tanaka, *J. Mol. Catal.*, 45 (1988) 91.
- [424] (a) J. Kiji, T. Okano, W. Nishiumi, H. Konishi, *Chem. Lett.*, (1989) 957; b) J. Kiji, T. Okano, H. Konishi, W. Nishiumi, *Chem. Lett.*, (1989) (1873); c) J. Tsuji, K. Sato, H. Okumoto, *J. Org. Chem.*, 49 (1984) 1341; d) D. Milstein, *Organometallics*, 1 (1982) 888; e) H.R. Gao, Y. Xu, S.J. Liao, D.R. Yu, *Chin. Chem. Lett.*, 3 (1992) 351.
- [425] (a) H. Alper, *Adv. Organomet. Chem.*, 19 (1981) 183; b) N. Satyanarayana, M. Periasamy, *Tetrahedron Lett.*, 28 (1987) 2633; c) F. Haasz, T. Bartik, V. Galamb, G. Palyi, *Organometallics*, 9 (1990) 2773; d) M.L. Kantam, N.P. Reddy, B.M. Choudary, *Synth. Commun.*, 20 (1990) 2631; e) S. Gambarotta, H. Alper, *J. Organomet. Chem.*, 212 (1981) C23.
- [426] J.-J. Brunet, C. Sidot, P. Caubere, *J. Org. Chem.*, 48 (1983) 1919.
- [427] G.W. Parshall, W.A. Nugent, *CHEMTECH*, (1988) 314.
- [428] (a) T. Okano, I. Uchida, T. Nakagaki, H. Konishi, J. Kiji, *J. Mol. Catal.*, 54 (1989) 65; b) T. Okano, N. Okabe, J. Kishi, *Bull. Chem. Soc. Jpn.*, 65 (1992) 2589; c) J. Kishi, T. Okano, W. Nishiumi, H. Konishi, *Chem. Lett.*, 6 (1988) 957; d) Rhone Poulenc (D. Sinou), EP 0.407.256; *Chem. Abstr.*, 114: 142638k.
- [429] (a) H. Alper, N. Hamel, D.J.H. Smith, J.B. Woell, *Tetrahedron Lett.*, 26 (1985) 2273; b) J.B. Woell, H. Alper, *Tetrahedron Lett.*, 25 (1984) 3791.
- [430] C. Buchan, N. Hamel, J.B. Woell, H. Alper, *Tetrahedron Lett.*, 26 (1985) 5743.
- [431] C. Buchan, N. Hamel, J.B. Woell, H. Alper, *J. Chem. Soc., Chem. Commun.*, (1986) 167.
- [432] R.A. Sawicki, *J. Org. Chem.*, 48 (1983) 5382.
- [433] H. Urata, N.-X. Hu, H. Maekawa, T. Fuchikama, *Tetrahedron Lett.*, 32 (1991) 4733.
- [434] (a) S.-I. Murahashi, Y. Imada, Y. Taniguchi, S. Shinya, *J. Org. Chem.*, 58 (1993) 1538; b) S.-I. Murahashi, Y. Imada, Y. Taniguchi, S. Higashiura, *Tetrahedron Lett.*, 29 (1988) 4945; c) Y. Koyasu, H. Matsuzaka, Y. Hiroe, Y. Uchida, M. Hidai, *J. Chem. Soc., Chem. Commun.*, (1987) 575; d) J. Kiji, T. Okano, I. Ono, H. Konishi, *J. Mol. Catal.*, 39 (1987) 355.
- [435] (a) J. Tsuji, *Tetrahedron*, 42 (1986) 4361; b) J. Tsuji, K. Sato, H. Okumoto, *J. Org. Chem.*, 49 (1984) 1341; c) J. Tsuji, K. Sato, H. Okumoto, *Tetrahedron Lett.*, 23 (1982) 5189; d) S.-Z. Wang, K. Yamamoto, H. Yamada, T. Takahashi, *Tetrahedron*, 48 (1992) 2333.
- [436] (a) D. Neibecker, J. Oirier, I. Tkatchenko, *J. Org. Chem.*, 54 (1989) 2459; b) M.C. Bonnet, D. Neibecker, B. Stitou, I. Tkatchenko, *J. Organomet. Chem.*, 366 (1989) C9; c) M.C. Bonnet, J. Coombes, B. Manzano, D. Neibecker, I. Tkatchenko, *J. Mol. Catal.*, 52 (1989) 263; d) A.S.C. Chan, *Chem. Eng. News*, 62 (1984) 28.
- [437] (a) Y. Imada, O. Shibata, S.-I. Murahashi, *J. Organomet. Chem.*, 451 (1993) 183; b) S.-I. Murahashi, Y. Imada, *Chem. Lett.*, 10 (1985) 1477.
- [438] (a) K. Itoh, N. Hamaguchi, M. Miura, M. Nomura, *J. Mol. Catal.*, 75 (1992) 117; (b) T. Imamoto, T. Kusumoto, A.M. Yokoya, *Bull. Chem. Soc. Jpn.*, 55 (1982) 643; c) G. Cavinato, L. Toniolo, *J. Mol. Catal.*, 78 (1993) 131.
- [439] T. Yamamoto, M. Akimoto, O. Saito, A. Yamamoto, *Organometallics*, 5 (1986) 1559.
- [440] (a) Ethyl Corp. (B.C. Stahly, R.W. Lin, E.E. Atkinson), US 4.990.658 (1989); *Chem. Abstr.*, 114: 246.962; b) Daicel Chem. Ind. (M. Kawabe, H. Kojima), JP 63.162.044 (1986); *Chem. Abstr.*, 109: 238.149; c) Daicel Chem. Ind. (Y. Tanaka, H. Kojima, Y. Tsuji, GB 2.199.030 (1986); *Chem. Abstr.*, 109: 212.807n; d) Nippon Petrochem. (I. Shimizu, Y. Matsumura, Y. Inomata, K. Uchida), JP 02.101.041 (1990); *Chem. Abstr.*, 113: 97.202e.
- [441] Hoechst Celanese Corporation (V. Elango, M.A. Murphy, G.L. Moss, B.L. Smith, K.G. Davenport, G.N. Mott), EP 0.284.310 (1988); *Chem. Abstr.*, 110: 153.916t; b) Hoechst AG (S. Rittner, A. Schmidt, L.O. Wheeler, G.L. Moss, E.G. Zey), EP 0.326.027 (1989); *Chem. Abstr.*, 112: 35.448k.
- [442] H. Arzoumanian, G. Buono, M.B. Choukrad, J.-F. Petignani, *Organometallics*, 7 (1988) 59.
- [443] J.M. Baird, J.R. Kern, G.R. Lee, D.J. Morgans, M.L. Sparacino, *J. Org. Chem.*, 56 (1991) (1928).
- [444] S.C. Shim, S. Antebi, H. Alper, *J. Org. Chem.*, 50 (1985) 147.
- [445] S.-I. Murahashi, Y. Imada, K. Nishimura, *J. Chem. Soc., Chem. Commun.*, (1988) 1578.
- [446] M. Miyazawa, S.-Z. Wang, H. Takeda, K. Yamamoto, *Synlett*, (1992) 323.
- [447] (a) Denki Kagaku Kogyo (K. Aoki, Y. Tabata, H. Hirano, T. Shimizui) JP 06.130.548; *Chem. Abstr.* 105: 42.480y; b) Kawaken Fine Chem. (A. Kasahara, T. Izumi) JP 61.027.937 (1984); *Chem. Abstr.*, 104: 224.570; c) A. Kasahara, T. Izumi, H. Yanai, *Chem. Ind. (London)*, 23 (1983) 898.
- [448] N.A. Bumagin, A.B. Ponomaryov, I.P. Beletskaya, *Tetrahedron Lett.*, 26 (1985) 4819.
- [449] a) F.K. Sheffy, J.P. Godschalx, J.K. Stille, *J. Am. Chem. Soc.*, 106 (1984) 4833; b) R. van Asselt, C.J. Elsevier, *Organometallics*, 11 (1992) (1999).
- [450] Y. Wakita, T. Yasunga, M. Akita, M. Kojima, *J. Organomet. Chem.*, 301 (1986) C17.
- [451] S. Katsumura, S. Fujiwara, S. Isoe, *Tetrahedron Lett.*, 29 (1988) 1173.
- [452] T. Kobayashi, M. Tanaka, *J. Organomet. Chem.*, 205 (1981) C27.
- [453] Y. Tamaru, K. Yasui, H. Takanabe, S. Tanaka, K. Fugami, *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 645.

- [454] (a) E.-I. Negishi, G. Wu, J.M. Tour, *Tetrahedron Lett.*, 29 (1988) 6745; b) A. Cowell, J.K. Stille, *J. Am. Chem. Soc.*, 107 (1980) 4193; c) Y. Tamaru, T. Bando, M. Hojo, Z. Yoshida, *Tetrahedron Lett.*, 28 (1987) 3497.
- [455] (a) Y. Koyasu, M. Matsukaza, Y. Hiroe, Y. Uchida, M. Hidai, *J. Chem. Soc., Chem. Commun.*, (1987) 575; b) H. Matsuzaka, Y. Hiroe, M. Iwasaki, Y. Ishii, Y. Koyasu, M. Hidai, *J. Org. Chem.*, 53 (1988) 3832; c) M. Iwasaki, Y. Kobayashi, J.-P. Li, H. Matsuzaka, Y. Ishii, M. Hidai, *J. Org. Chem.*, 56 (1991) (1922).
- [456] W. Oppolzer, *Pure Appl. Chem.*, 62 (1990) (1941).
- [457] (a) W. Oppolzer, T.H. Keller, M. Bedoya-Zurita, C. Stone, *Tetrahedron Lett.*, 30 (1989) 5883; b) W. Oppolzer, T.H. Keller, D.L. Kuo, W. Pachinger, *Tetrahedron Lett.*, 31 (1990) 1265.
- [458] J. Ji, X. Lu, *Tetrahedron*, 50 (1994) 9067.
- [459] N. Benard, M.C. Bonnet, S. Lecolier, I. Tkatchenko, *J. Chem. Soc., Chem. Commun.*, (1993) 1448.
- [460] J.F. Knifton, *J. Organomet. Chem.*, 188 (1980) 223.
- [461] (a) H. Alper, D. Leonard, *Tetrahedron Lett.*, 26 (1985) 5639; b) H. Alper, N. Hamel, *J. Chem. Soc., Chem. Commun.*, (1990) 135.
- [462] B.E. Ali, H. Alper, *J. Org. Chem.*, 56 (1991) 5357.
- [463] a) P. Chaumette, F. Hugues, *Rev. Inst. Franc. Petr.*, 40 (1985) 91; b) J. Kollar, *CHEMTECH*, 14 (1984) 504.
- [464] Reviews: a) M. Marchionna in, *Oxygenates by Homologation or CO Hydrogenation with Metal Complexes*, Ed., G. Braca, Kluwer Academic Publ. Dordrecht, 1994; b) G.A. Korneeva, S.M. Loktev, *Russ. Chem. Rev.*, 58 (1989) 73.
- [465] E. Drent, *Pure Appl. Chem.*, 62 (1990) 661.
- [466] S.Y. Lee, J.C. Kim, J.S. Lee, Y.G. Kim, *Ind. Eng. Chem. Res.*, 32 (1993) 253.
- [467] G. Cavinato, L. Toniolo, *J. Mol. Catal.*, 69 (1991) 283.
- [468] (a) J.F. Knifton, J.J. Lin, D.A. Storm, S.F. Wong, *Catal. Today*, 18 (1993) 355; b) J.J. Lin, J.F. Knifton in W.R. Moser, D.W. Slocum (Eds.), *Homogeneous Transition Metal Catalyzed Reaction, Advances in Chemistry Series No. 230, Chapter 16*, ACS, Washington, 1992; c) I. Ojima, *Chem. Rev.*, 88 (1988) 1011; d) J.J. Lin, J.F. Knifton, *CHEMTECH*, (1992) 248.
- [469] H. Wakamatsu, J. Uda, N. Yamakami, *J. Chem. Soc., Chem. Commun.*, (1971) 1540.
- [470] J.J. Lin, J.F. Knifton, *J. Organomet. Chem.*, 147 (1991) 99.
- [471] K. Izawa, *J. Mol. Catal.*, 41 (1987) 135.
- [472] P. Magnus, M. Slater, *Tetrahedron Lett.*, 28 (1987) 2829.
- [473] M. Beller, H. Fischer, P. Groß, T. Gerdau, DE 4.415.712 (1994).
- [474] I. Ojima, *J. Mol. Catal.*, 37 (1986) 25.
- [475] I. Ojima, K. Hirai, M. Fujita, T. Fuchikami, *J. Organomet. Chem.*, 279 (1985) 203.
- [476] K. Hirai, Y. Takahashi, I. Ojima, *Tetrahedron Lett.*, 23 (1982) 2491.
- [477] (a) Y. Amino, K. Izawa, *Bull. Chem. Soc. Jpn.*, 64 (1991) 613; b) I. Ojima, M. Okabe, K. Kato, H.B. Kwon, I.T. Horvath, *J. Am. Chem. Soc.*, 110 (1988) 150; c) Institute Francais du Petrole (R. Stern, A. Hirschauer, D. Commereuc, Y. Chauvin), US Patent 4.264.515 (1981).
- [478] (a) T. Sakakura, X.-Y. Huang, M. Tanaka, *Bull. Chem. Soc. Jpn.*, 64 (1991) 1707; b) S. Takigawa, S. Shinke, M. Tanaka, *Chem. Lett.*, (1990) 1415.
- [479] I. Ojima, Z. Zhang, A. Korda, P. Ingallina, N. Clos in W.R. Moser, D.W. Slocum (Eds.), *Homogeneous Transition Metal Catalyzed Reaction, Advances in Chemistry Series No. 230, Chapter 19*, ACS, Washington (1992).
- [480] Reviews: a) S. Cenini, C. Grotti, M. Pizzotti in, *Aspects of Homogeneous Catalysis*, Vol. 6, p. 97, R. Ugo, D. Reidel Publishing Company (1988); b) S. Cenini, C. Grotti, *Catal. Met. Complexes*, 12 (1991) 311.
- [481] (a) R. Ugo, R. Psaro, M. Pizzotti, P. Nardi, C. Dossi, A. Andreatta, G. Capparella, *J. Organomet. Chem.*, 417 (1991) 211; b) N.P. Reddy, A.M. Masdeu, B. El Ali, H. Alper, *J. Chem. Soc., Chem. Commun.*, (1994) 863; c) V.L.K. Valli, H. Alper, *J. Am. Chem. Soc.*, 115 (1993) 3778; d) P. Leconte, F. Metz, A. Mortreux, J.A. Osborn, F. Paul, F. Petit, A. Pillot, *J. Chem. Soc., Chem. Commun.*, (1990) 1616; e) P. Wehman, G.C. Dol, E.R. Moorman, P.C.J. Kamer, P.W.N.M. Leeuwen, *Organometallics*, 13 (1994) 4865; f) Mitsui Toatsu Chemicals (E. Takagi, K. Inoue, K. Ikeda, R. Tsumora), JP 94.011.745 (1994).
- [482] (a) S. Cenini, F. Ragaini, M. Pizzotti, F. Porta, G. Mestroni, E. Alessio, *J. Mol. Catal.*, 64 (1991) 179, b) F. Ragaini, S. Cenini, F. Demartin, *Organometallics*, 13 (1994) 1178; c) C.V. Rode, S.P. Gupte, R.V. Chaudari, C.D. Pirozhkov, A.L. Lapidus, *J. Mol. Catal.*, 91 (1994) 195.
- [483] (a) S.J. Skoog, J.P. Campbell, W.L. Gladfelter, *Organometallics*, 13 (1994) 4137; b) J.D. Gargulak, W.L. Gladfelter, *J. Am. Chem. Soc.*, 116 (1994) 3792; c) Hercules Corp. (J.H. Grate, D.R. Hamm, D.H. Valentine), US 04.600.7 93 (1986).
- [484] J. Sundermann, H.J.S. Scholl in B. Cornils, W.A. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Complexes*, VCH Verlag Chemie, Weinheim, 1996.
- [485] K. Kaneda, H. Kuwahara, T. Imanaka, *J. Mol. Catal.*, 88 (1994) L267.
- [486] (a) H. Alper, F.W. Hartstock, *J. Chem. Soc., Chem. Commun.*, (1985) 1141; b) H. Alper, G. Vasapollo, F.W. Hartstock, M. Mlekuz, D.J.H. Smith, G.E. Morris, *Organometallics*, 6 (1986) 2391.
- [487] P. Giannoccaro, *J. Organomet. Chem.*, 336 (1987) 271; d) S. Fukuoka, M. Chono, M. Kohno, *J. Org. Chem.*, 49 (1984) 1458.
- [488] P. Giannoccaro, *J. Organomet. Chem.*, 470 (1994) 249.
- [489] F.W. Hartstock, D.G. Herrington, L.B. McMahn, *Tetrahedron Lett.*, 35 (1994) 8761.

- [490] T.W. Leung, B.D. Dombek, *J. Chem. Soc., Chem. Commun.*, (1992) 205.
- [491] (a) A. Bassoli, B. Rindone, S. Tollari, F. Chioccare, *J. Mol. Catal.*, 60 (1990) 41; (b) G. Mandinelli, M. Nali, B. Rindone, S. Tollari, *J. Mol. Catal.*, 39 (1987) 155.
- [492] (a) M.M. Taqui Khan, S.B. Halligudi, S.H.R. Abdi, *J. Mol. Catal.*, 48 (1988) 325; (b) M.M. Taqui Khan, S.B. Halligudi, S.H.R. Abdi, S. Shukla, *J. Mol. Catal.*, 48 (1988) 25.
- [493] M.M. Taqui Khan, S.B. Halligudi, N. Shukla, *J. Mol. Catal.*, 59 (1990) 303.
- [494] S.-K. Kang, Y.-W. Park, D.H. Lee, H.-S. Sim, J.-H. Jeon, *Tetrahedron Asymm.*, 3 (1992) 1139.
- [495] G. Bensenyei, S. Nimeth, L.I. Simandi, *Angew. Chem. Int. Ed. Engl.*, 29 (1990) 1147.
- [496] M. DeWang, H. Alper, *J. Am. Chem. Soc.*, 114 (1992) 7018.
- [497] J. Haggin, *Chem. Eng. News*, 65 (1987) 27.
- [498] A. Chauvel, B. Delmon, W.F. Hölderich, *Appl. Catal.*, 115 (1994) 173.
- [499] Enichem (U. Romano, F. Rivetti, N. Di Muzio), US 4.318.862 (1982).
- [500] Bayer AG (H.J. Buysch), US 4.434.105 (1984).
- [501] Ube Industries (N. Nishimura, K. Fujii, K. Nishihira, M. Matsuda, S. Uchiumi), US 4.229.591 (1980).
- [502] Ube Industries (N. Nishimura, S. Uchiumi, K. Fujii, K. Nishihira, M. Yamashita, H. Itatani), US Patent, 04.229.589 (1980).
- [503] J.B. Saunby, Ethylene Glycol from Syngas, in *Carbon One Chemical Technology – The future route to fuels and chemical feedstocks?*, The Institution of Chemical Engineers, Rugby, 1986, p. 153.
- [504] (a) M. Lin, A. Sen, *J. Chem. Soc., Chem. Commun.*, (1992) 892; (b) A. Sen, M. Lin, *J. Chem. Soc., Chem. Commun.*, (1992) 508; (c) D.H.R. Barton, D. Doller, *Acc. Chem. Res.*, 25 (1992) 504; (d) D.H.R. Barton, E. Cshui, D. Doller, *Tetrahedron Lett.*, 33 (1992) 4389; (e) W.T. Boese, A.S. Goldman, *J. Am. Chem. Soc.*, 114 (1992) 350.
- [505] A.J. Kunin, R. Eisenberg, *Organometallics*, 7 (1988) 2124.
- [506] M. Tanaka, T. Sakakaru, H. Wada, Y. Sasaki, JP 01.249.741 (1989); *Chem. Abstr.*, 112: (1990) 98.197.
- [507] E.J. Moore, W.R. Pretzer, T.J. O'Connell, J. Harris, L. Labounty, L. Chou, S.S. Grimmer, *J. Am. Chem. Soc.*, 114 (1992) 5888.
- [508] K. Nakata, T. Miyata, T. Jintoku, A. Kitani, Y. Taniguchi, K. Takaki, Y. Fujiwara, *Bull. Chem. Soc. Jpn.*, 66 (1993) 3755.
- [509] S. Tsunoi, I. Ryu, N. Sonuda, *J. Am. Chem. Soc.*, 116 (1994) 5473.
- [510] (a) I. Ryu, K. Nagahara, H. Yamazaki, S. Tsunoi, N. Sonuda, *Synlett*, (1994) 643; (b) I. Ryu, H. Alper, *J. Am. Chem. Soc.*, 115 (1993) 7543; (c) I. Ryu, H. Yamazaki, A. Ogawa, N. Kambe, N. Sonuda, *J. Am. Chem. Soc.*, 115 (1993) 1187.
- [511] (a) M. Misono, N. Nojiri, *Appl. Catal.*, 64 (1990) 1; (b) N. Nojiri, M. Misono, *Appl. Catal.*, 93 (1993) 103.
- [512] M. Komatsu, *Petrotech (Japan)*, 10 (1986) 632.
- [513] Mitsubishi Gas Chemical (T. Tanaka, M. Inari), JP 01.265.056 (1989).
- [514] (a) A.M. Viturtia, J. Mata-Alvarez, C. Sans, J. Costa, F. Cecchi, *Environmental Technol.* (1992), 13, 1033; (b) Elefsiniotis, W.K. Oldham, *Biotechnol. Bioeng.*, 44 (1994) 7.
- [515] Standard Oil Comp. (N.C. Benkalowycz, P.R. Blum, R. Wagner), US 5.300.684 (1994); BP (M. Kitson), US 5.260.250 (1991).
- [516] Europa-Chemie, (52) (1992) 5; Europa-Chemie, (37) (1993) 4; Europa-Chemie, (11) (1994) 7.
- [517] e.g. Ethyl Corp. (G. Wilkinson), US 3.501.531 (1970); J.K. Stille, G. Parinello, PCT/WO 88/08835 (1988); C.-Y. Hsu, M. Orchin, *J. Am. Chem. Soc.*, 97 (1975) 3553; P.W.N.M. van Leeuwen, C.F. Roobeek, *New J. Chem.*, 14 (1990) 487; J.K. Stille, H. Su, P. Brechot, G. Parrinello, L.S. Hegedus, *Organometallics*, 10 (1991) 1183.
- [518] Anonymous, *Chemical Week*, July 27 (1994) 26.
- [519] Hoechst AG, (H. Erpenbach, K. Gehrmann, E. Jägers, G. Koch), DE 3.823.645 (1989); (H. Erpenbach, K. Gehrmann, P. Hörstermann, K. Schmitz), EP 0.170.964 (1988).
- [520] (a) Anonymous, ECN Int. Project Review, Part 1, March (1990); (b) Hoechst AG, Press Release No. 0103 of Sept. 1 (1992) and 0178 of Nov. 29 (1989).
- [521] e.g. B. Gronewold, D. Hesse, *Chem. Ing. Techn.*, 67 (1995) 82.
- [522] J. Haggin, *Chem. Eng. News*, April 17 (1995).