

Review

Recent developments in aqueous organometallic chemistry and catalysis

Ferenc Joó^{*}, Ágnes Kathó

Institute of Physical Chemistry, Lajos Kossuth University, P.O. Box 7, Debrecen, H-4010, Hungary

Received 5 February 1996; accepted 29 February 1996

Abstract

A survey of the literature published in 1995 and partly in 1994 on organometallic chemistry and catalysis shows that the field is characterized by further dynamic progress in research of industrially relevant processes, such as hydroformylation, in extension of aqueous organometallic catalysis to more and more diverse laboratory syntheses and in understanding the mechanisms of such processes.

Keywords: Catalysis; Organometallic; Aqueous; Water soluble; Phosphines; Transition metals; Hydroformylation; Hydrogenation; Coupling; Heterogenization

1. Introduction

Following a long induction period, organometallic catalysis in aqueous systems became a most actively studied field of research recently. This is indicated by two recent specialized meetings, a NATO Advanced Research Workshop (Debrecen, Hungary, 1994) and a special workshop on aqueous organometallic chemistry and catalysis at the 209th Meeting of the American Chemical Society (Anaheim, CA, 1995). The proceedings of the former conference, including the evaluation of the state of the art of the field, have been published [1] and the material of the latter workshop is contained in

the abstract volume of the ACS meeting [2]. In addition, following earlier surveys [3–6], since 1991 a new review appeared each year [7–11], and a forthcoming book on industrial homogeneous catalysis also treats aqueous organometallic catalysis extensively [12]. Progress in hydroformylation and carbonylation has been reviewed in late 1995 [13]. The first hydroformylation plant using an aqueous–organic biphasic process went on stream in 1984 and the experience gained since then and some conclusions of the intensive research accompanying the first ten years of operation are discussed in three papers [14–16]. A forthcoming volume of *Inorganic Syntheses* devotes considerable space to water soluble organometallic complexes [17]. The special questions of application of organometallic catalysis for the modification of

^{*} Corresponding author.

biomembranes [18], of organometallic aqua ions of transition metals [19], of the chemistry of clusters in aqueous media [20], and of application of biphasic processes in synthesis of vitamins A and E [21] have also been reviewed recently.

With such an abundance of reviews the contents of the present paper is limited to the description of the very latest developments, published mostly in 1995 or in the second part of 1994, with only a very few references to earlier results. This special issue of Journal of Molecular Catalysis will undoubtedly further complement and modify the picture which can be shown based on the results of 1994/95.

2. Synthesis of new water soluble ligands

One of the earliest and still useful strategies of obtaining water soluble ligands for organometallic catalysis is the attachment of ionic or polar substituents to known ligands of active transition metal catalysts. However, in many cases, direct functionalization of the ligands poses severe problems with respect to the precise control of the number and position of the substituents. A showcase of such problems is sulfonation which is by far the most widely used method of rendering organic ligands water soluble; for example, the reaction of triphenylphosphine with fuming sulfuric acid should be monitored and strictly controlled to achieve reasonable purity of the possible products, TPPMS (**1**), TPPDS (**2**) or TPPTS (**3**) and to avoid oxidation. Therefore, the latest developments in producing water soluble ligands for organometallic catalysis are characterized by improvements of direct functionalizations, by a diversity of the ionic or polar substituents introduced, and by more and more extensive application of ingenious methods of organic chemistry to build up tailor-made water soluble molecules without prior synthesis of the corresponding non-ionic or non-polar analogs. Examples of water soluble phosphines are shown in Fig. 1.

The most important development in direct functionalization is the new method [22] of Herrmann et al. for the sulfonation of arylphosphines and arylphospholes in a superacidic medium made up from orthoboric acid and anhydrous sulfuric acid. Owing to the extremely high acidity of the system all phosphorus(III) compounds are completely quaternized, and, in contrast to oleum, such sulfonation mixtures do not contain free SO_3 . As a consequence of these two factors oxidation of phosphorus is avoided. Another important feature of such sulfonations is that the number and position of sulfonate groups is more uniform than in case of sulfonations with fuming sulfuric acid. Such way the reaction of triphenylphosphine could be optimized to give either TPPDS or TPPTS with negligible oxidation. Also, tri-*o*-tolylphosphine, tri-*o*-anisylphosphine, 2,2'-bis(diphenylphosphinomethyl)1,1'-binaphthyl and even 5-phenyl-5*H*-dibenzophosphole was subjected to precision sulfonation yielding the highly water soluble, uniform products **4**, **5**, and **6**, respectively.

Stelzer and coworkers have developed a general method [23–26] for the synthesis of 4-sulfophenylphosphines (e.g., **7**) based on the reaction of 4-fluorobenzenesulfonates with PH_3 , primary, or secondary phosphines in strongly basic solutions. A comparison of 4-sulfophenylphosphines with the widely used 2-sulfonated arylphosphines (such as TPPMS and TPPTS) both with respect to their complex forming ability and catalytic properties could bring interesting discoveries.

Several new phosphines were synthesized and/or made water soluble by controlled sulfonation in fuming sulfuric acid, such as the bidentate 1,2-bis[di(3-sulfonatophenyl)phosphino]ethane, **8** [27], 1,3-bis[di(3-sulfonatophenyl)phosphino]propane, **9** [28], and the optically active bis[8-(4-sulfonatophenyl)octyl](menthyl)phosphine, **10** [29].

PH_3 reacts with $\text{Me}_2\text{N}(\text{CH}_2)_2\text{Cl}$ in DMSO–KOH to give the primary phosphine, $\text{H}_2\text{P}(\text{CH}_2)_2\text{NMe}_2$ which can be further con-

verted to $P[(CH_2)_2NMe_2]_3$ [25]. Upon protonation the latter affords the extremely water soluble tertiary phosphine ligand $\{P[(CH_2)_2NHMe_2]_3\}Cl_3$ (**11**, solubility 1450 g/1000 ml H_2O ; 20°C). Several Rh^I , Pd^{II} , W^0 and Fe^0 complexes of these ligands have been prepared and structurally characterized.

Free radical reactions of monodentate and bidentate phenylphosphines with alkynols, alkyne ethers, unsaturated carboxylic esters and beta-lactones afforded a variety of mono- and bidentate tertiary phosphines having hydroxy, ether or carboxy substituents some of which were water soluble [30].

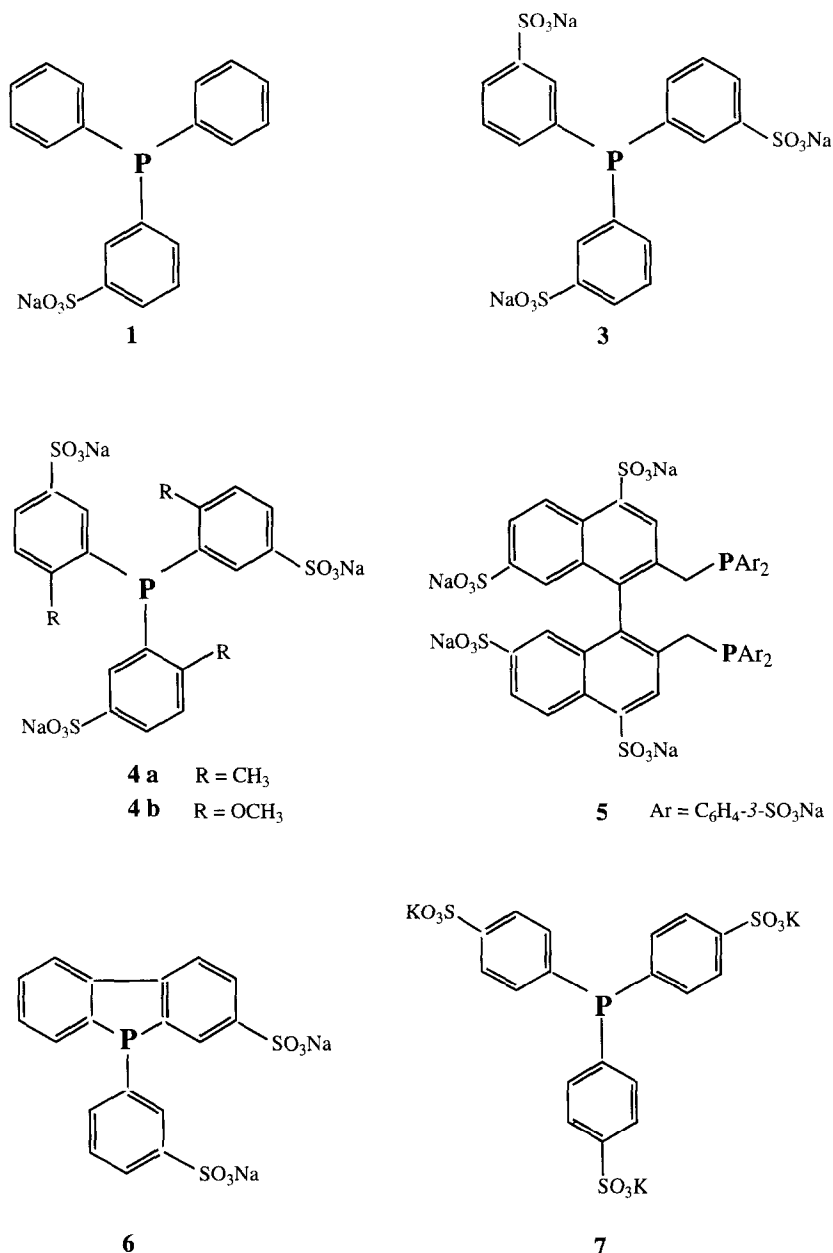


Fig. 1. Water soluble tertiary phosphines.

Alkali metal phosphides continued to serve as useful intermediates in the synthesis of new water soluble phosphines in their reactions with appropriate organic halides. A general method for the synthesis of carboxyphenylphosphines has appeared [31]. Chiral tertiary arylphos-

phines, such as the atropisomeric, tetrasulfonate (*R*)- or (*S*)-MeO-BIPHEP-TS (**12**) [32] and the surfactant sulfonate derivative (**13**) of 2,4-bis(diphenylphosphino)pentane [33], both containing the sulfonate group in 4-position relative to the phosphorus were prepared by this proce-

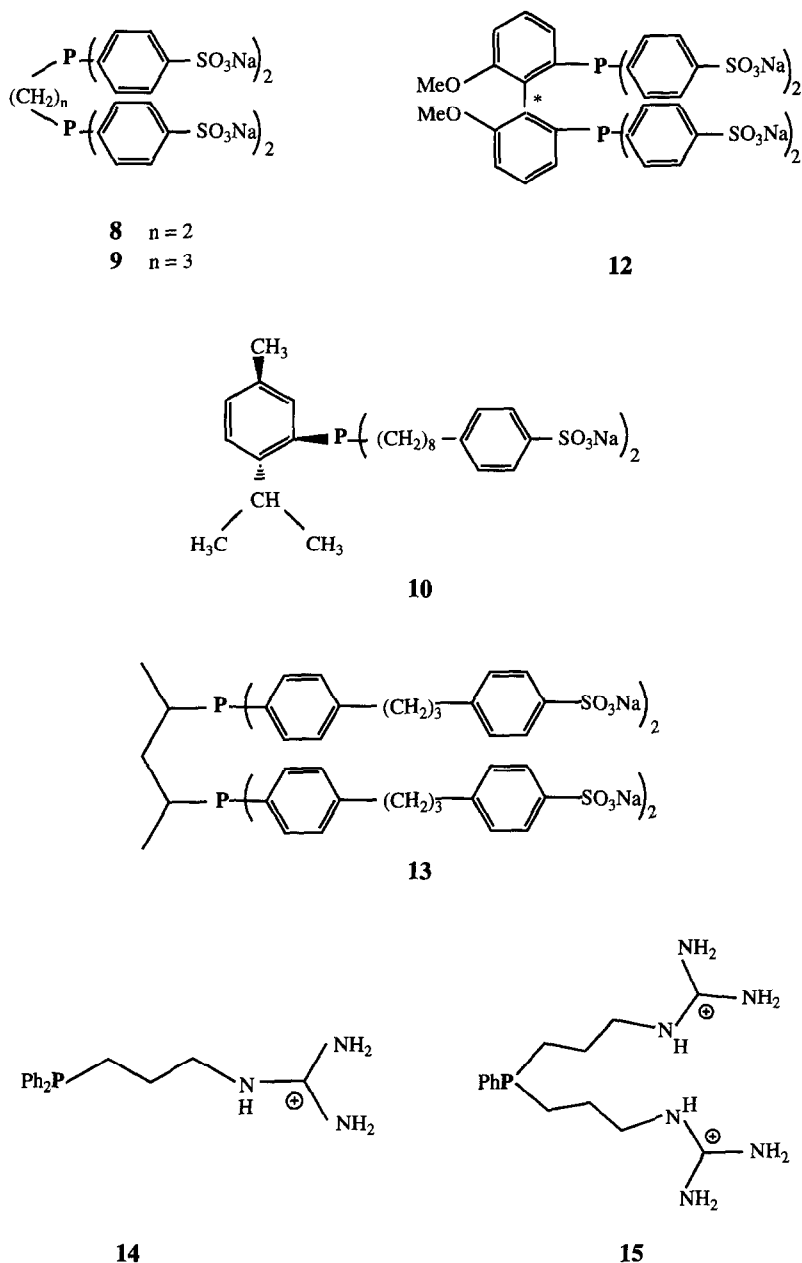


Fig. 1 (continued).

ture, as well as the highly water soluble cationic guanidino-phosphines, **14** and **15** [34]. Tertiary arylphosphines (**16**) containing one or two benzylic amino groups of different basicity have also been synthesized and used in hydroformylation studies [35]. Reaction of LiPPh_2 with $\text{CH}_2=\text{CH}-\text{CONHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{H}$ or with

itaconic acid yielded PNS (**17**) and PC (**18**), respectively, also tested in hydroformylation of methyl acrylate [36].

Diphenylphosphino-alkylphosphonates (**19**, **20**) [37,38], diphenylphosphino-arylphosphonates (**21**) [39] and their Pt^{II} and Pd^{II} complexes have been prepared and charac-

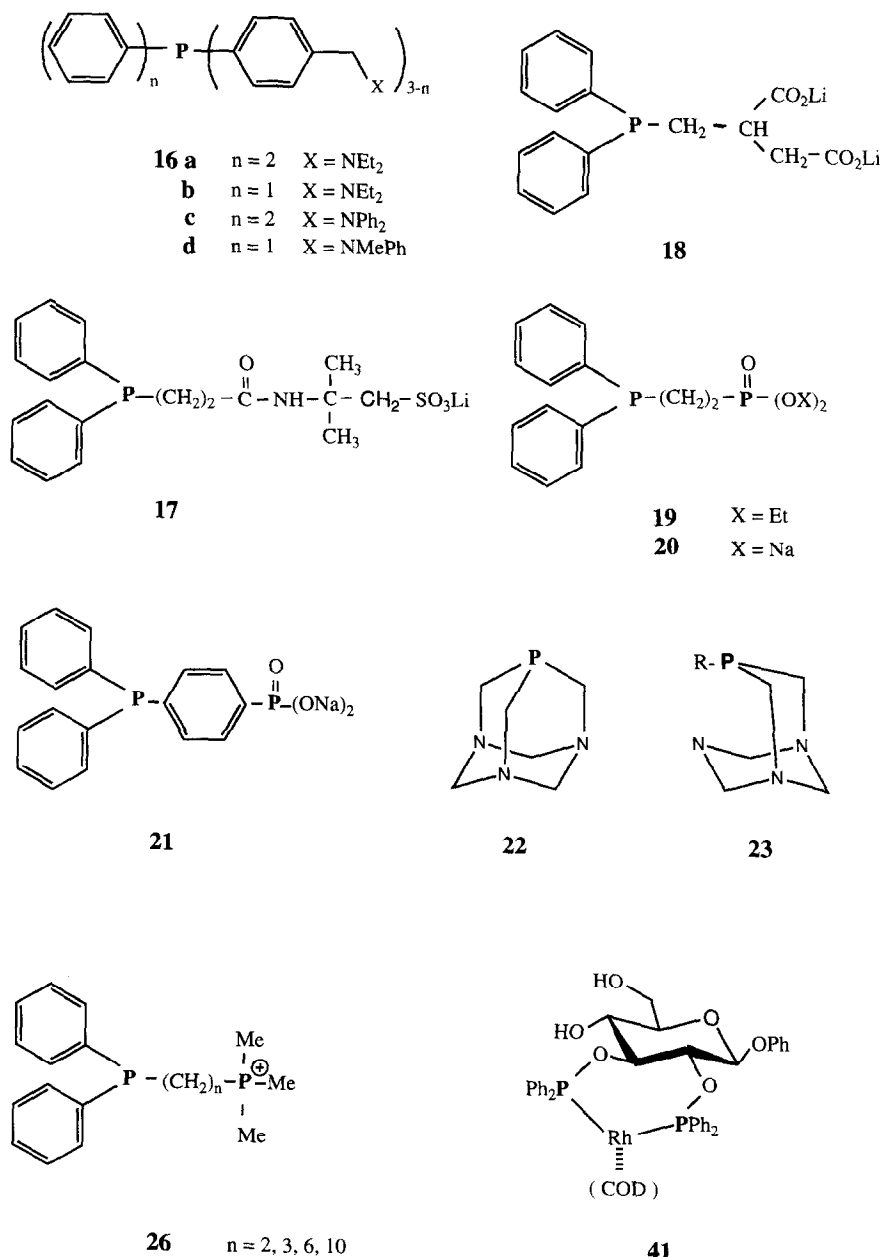


Fig. 1 (continued).

terized, including the X-ray structure determination of *trans*-[PdBr₂(**19**)₂]. Some of the palladium complexes have been investigated as catalysts for olefin hydration. ³¹P-NMR spectroscopy permits the separate investigation of the non-coordinating phosphonate and the ligating phosphorus atoms; by this way the effects of changes in the state of the central metal ion during catalysis, and the general effects of the environment on the phosphorus signals can be studied separately.

Reaction of 1,3,5-triaza-7-phosphaadamantane (PTA, **22**) with alkyl halides is known to yield *N*-alkylated ammonium salts. The *P*-alkylated phosphonium salts were synthesized [40,41] from the readily available tris(hydroxymethyl)phosphonium derivatives, and underwent reductive cleavage by sodium in liquid NH₃ to afford the potentially *P,N*-bidentate phosphine **23**, the coordination properties of which await further study.

3. Preparation and characterization of water soluble organometallic and related complexes

Rhodium and ruthenium complexes of the type RhCl(CO)L₂, (*L* = PTA, **22**; P(CH₂OH)₃, **24**; P(CH₂CH₂CN₃)₃, **25**), RuCl₂L₃ and RuCl₂(CO)₂L₂ (*L* = **25**) were isolated and characterized [42]. RhCl(CO)(**24**)₂ and RhCl(CO)(PTA)₂ were found relatively active catalysts of the water gas shift reaction at 343 K (TO = 6 mol H₂/h mol Rh). Most interestingly the aqueous system prepared in situ from Rh₂(OAc)₄(H₂O)₂ and PTA (1:3) catalyzed the hydrogenation of CO₂ both to CO and CH₄, an unusual product mixture in homogeneous CO₂ reductions.

A one-step synthesis of the cationic [PdCl(TPPTS)₃]⁺ was described [43]. The reaction of PdCl₂ and TPPTS was monitored by ¹⁷O-, ¹H/³¹P- and ³⁵Cl-NMR spectroscopy. [PdCl(TPPTS)₃]⁺ is isoelectronic with RhCl(PPh₃)₃ which promises high reactivity towards small molecules. This is in fact observed

in the very fast reduction of the complex to Pd(TPPTS)₃ by CO (5 min) as compared to the reduction by excess TPPTS (8 days), both at 25°C. ¹⁷O-NMR can especially be useful for the direct study of hydroxo complexes formed by metal ion hydrolysis in aqueous solutions.

A new route for the synthesis of HRu(CO)Cl(TPPMS)₃ · 2H₂O has been worked out which yields a more uniform product than obtained in previous syntheses [44]. The complex was found stable in aqueous solution at normal temperature and pressure for at least for a day, that is no hydrolysis of the compound occurred. Hydrogenation of styrene, 1-cyclohexene in water/decalin 1/1 mixtures proceeded rather slowly at 100°C and 1000 psi, turnover frequencies being 3.0 and 1.1 h⁻¹, respectively. The catalyst was shown stable under the conditions of hydrogenation, too.

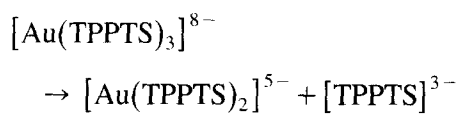
The water soluble analog of Vaska's compound, *trans*-IrCl(CO)(TPPMS)₂ and related complexes were prepared, characterized and used as catalyst in isomerization studies [45,46].

A continuing study of 2-pyridylphosphine complexes [47] have shown that some of the Ni^{II} and Ni⁰ compounds, NiBr₂[d(py)pe] and Ni(CO)₂[d(py)pe] are water soluble but exhibit complex solution behavior and decomposition in water. A detailed synthesis of the ligand, d(py)pe = py₂PCH₂CH₂Ppy₂, py = 2-pyridyl, has also been published.

Fe₂(CO)₉ reacted with the cationic phosphonium phosphines (*n*-phosphos, **26**) [Ph₂P(CH₂)_nPMe₃]⁺, *n* = 2,3,6 and 10, to yield complexes of the type Fe(CO)₄L, which were isolated and characterized [48]. Though *trans*-Fe(CO)₃L₂ could not be isolated in pure form it was unambiguously characterized as a byproduct of Fe(CO)₄L syntheses. [CpFe(CO)₂L]⁺ complexes were obtained by oxidation of [CpFe(CO)₂]₂ by ferricinium ion ([Cp₂Fe]PF₆) in the presence of the appropriate phosphos ligand.

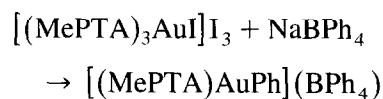
A series of papers [49–53] describes the preparation, characterization and photophysical properties of gold complexes with the water

soluble ligands TPPTS (**3**) and PTA (**22**). Among those the three coordinate $[\text{Au}(\text{PTA})_3]^+$ (**27**) and $[\text{Au}(\text{TPPTS})_3]^{8-}$ (**28**) are the first examples of gold(I) complexes which show strong luminescence in aqueous solution in the visible range upon UV excitation. The PTA ligands in **27** can be protonated on one of their nitrogen atoms and this has a strong influence on the luminescent properties (maximum luminescence observed at pH 10). Such pH dependence is absent with **28**, however its luminescence depends strongly on the solvent: when methanol, ethanol or acetone is added to aqueous solutions of this complex the intensity of luminescence decreases. It is believed, that in aqueous solution $[\text{Au}(\text{TPPTS})_3]^{8-}$ is stabilized by hydrogen bonding and electrostatic interactions similar to the case of Fe- [54] and Rh-complexes [55] described earlier. In less aqueous solutions dissociation



occurs diminishing the concentration of the luminescent three-coordinate compound.

Reaction of $[(\text{MePTA})_3\text{Au}]\text{I}_3$, containing the *N*-methyl derivative of PTA, and of **27** with NaBH_4 results in formation of phenylgold complexes:



Although similar reactions of tetraphenylborate are known, these reactions represent the first phenyl-transfer to gold(I) in aqueous solutions.

Studies in bioorganometallic chemistry have produced exciting new discoveries [56–59] on the synthesis and reactivity of complexes containing biologically important ligands (nucleobases, nucleosides and nucleotides) and the $\text{Cp}^*\text{Rh}^{\text{III}}$ moiety ($\text{Cp}^* = \text{pentamethylcyclopentadienyl}$). A literature confusion was removed by careful investigations on

the structure and dynamics of formation of $\eta^5\text{-Cp}^*\text{Rh}$ -aqua complexes as a function of pH. It was established [56] that $[\text{Cp}^*\text{Rh}(\text{H}_2\text{O})_3](\text{OTf})_2$ (**29**; $\text{OTf} = \text{trifluoroacetate}$) is stable at pH 2–5 but transforms to $[(\text{Cp}^*\text{Rh})_2(\mu\text{-OH})_3](\text{OTf}/\text{OH})$ (**30**) in alkaline solutions, being the only species present at pH 7–10. Although a $[(\text{Cp}^*\text{Rh})_2(\mu\text{-OH})(\text{H}_2\text{O})_2](\text{OTf})_2$ was postulated as an intermediate of this reaction, only one pK_a for the **29/30** equilibrium could be established by potentiometry ($pK_a = 5.3$). The structure of $[\text{Cp}^*\text{Rh}(\text{H}_2\text{O})_3](\text{OTf})_2$ was determined by X-ray diffraction. Reaction of **29** with the nucleobases 9-methyl- or 9-ethylhypoxanthine (9-MH and 9-EH, respectively) yielded the complexes $[\text{Cp}^*\text{Rh}(\eta^1(N^7)\text{-9-MH})(\text{MeOH})_2](\text{OTf})_2$ (pH 2.45–5.13), $[(\text{Cp}^*\text{Rh}[\mu^2\text{-}\eta^1(N^1):\eta^2(N^7,O^6)\text{-9-EH}]]_3(\text{OTf})_3$ (pH 6.45) and $[(\text{Cp}^*\text{Rh}[\eta^1(N^1)\text{-9-MH}](\mu\text{-OH})_2]$ (pH 10.5), showing unique coordination modes of the ligands [57]. Surprisingly, reaction of **30** with 1-methylthymine (1-MT), afforded the unique, two-coordinated Rh^{I} complex, $[\text{Rh}(\eta^1(N^3)\text{-1-MT})_2]^-$ (**31**) [58]. X-ray diffraction studies revealed a linear N–Rh–N coordination (bond angle 178.2°) and a near staggered configuration of the two thymine planes. An electrostatic interaction of anionic **31** and cationic **30** is further supplemented by a $\pi\text{-}\pi$ interaction between the thymine and the Cp^* planes making the complex $[\text{31}_2\text{30}_3]\text{OH}$ stable both in the solid state and in aqueous solution. The highly unsaturated nature of **31** is suspected to manifest itself in pronounced reactivity towards small molecules (CO , H_2 , CH_4). Cyclic trimers of complexes containing the Cp^*Rh moiety and a nucleobase, nucleoside, or nucleotide ligands showed the first example of molecular recognition of aromatic amino acid guests by bioorganometallic hosts in aqueous media at pH 7 [59]. $[\text{Cp}^*\text{Rh}(\text{9-methyladenine})_3](\text{OTf})_3$ (**32**), $[\text{Cp}^*\text{Rh}(\text{adenosine})_3](\text{OTf})_3$ (**33**), $[\text{Cp}^*\text{Rh}(\text{2'-deoxyadenosine})_3](\text{OTf})_3$ (**34**), and $[\text{Cp}^*\text{Rh}(\text{methyl-5'-adenosine monophosphate})_3]$ (**35**) are all stable in aqueous solutions for weeks at physiological

Table 1
Estimated association constants (K_a) of aromatic amino acids with cyclic rhodium-trimers 32–35

| Host | K_a (M^{-1}) | | | |
|-------|--------------------|-----|------|------|
| | 32 | 33 | 34 | 35 |
| Guest | | | | |
| L-phe | 16 | 12 | < 10 | < 10 |
| L-trp | 43 | 472 | 607 | < 10 |

pH and show preferential binding of aromatic amino acids, such as L-phenylalanine (L-phe) and L-tryptophan (L-trp) over the non-aromatic amino acids which were negligibly complexed or not at all. Association constants for 1:1 host:guest complexes were determined at ambient temperature by a standard NMR method based upon the complexation induced 1H -NMR chemical shifts of both hosts and guests and are shown in Table 1.

Aqua complexes of rhodium and ruthenium have attracted increasing interest recently, generated in a large part by the outstandingly useful catalytic properties of $[Ru(H_2O)_6]^{2+}$ in the ring opening metathesis polymerization of cyclic strained olefins. Rhodium(I) aqua complexes of the type $[L_2Rh(H_2O)_2]^+$ and $[(LL)Rh(H_2O)_2]^+$ (L = cyclooctene, ethylene; LL = cyclooctadiene (COD), norbornadiene, 2-methyl-1,3-butadiene or 2,3-dimethyl-1,3-butadiene) were prepared by chloride removal (Ag^+) from the corresponding dimers $[L_2RhCl]_2$ and $[(LL)RhCl]_2$ in aqueous acetone as solvent [60]. The rate constant of water exchange in $[(COD)Rh(H_2O)_2]^+$ was determined as $k = 10^4 s^{-1}$ at 173 K. Although the bis(aqua) complexes could not be crystallized properly, the structure of $(COD)Rh(H_2O)(\eta^1-OTs)$ was determined by X-ray diffraction (OTs = toluene-4-sulfonate).

Optically active amino acidato complexes of the types $[Cp^*M(aa)Cl]$ and $[Cp^*M(aa)(PPh_3)]BF_4$ (aa = amino acidate, M = Rh, Ir) in which the metal is a chiral center, have been prepared and characterized. Most of these complexes are water soluble and show potential for asymmetric synthesis and catalysis, e.g., in enantioselective reduction of ketones by

hydrogen transfer from wet or aqueous 2-propanol. The crystal structure of the acetylide derivative $(R_{Ir}, S_N, S_C)-[Cp^*Ir(L-prolinate)(C\equiv C-CMe_3)]$ has been reported [61].

Unsaturated cyclic ketones undergo aromatization when heated with $[Ru(H_2O)_6](OTs)_2$ or with $[(benzene)Ru(H_2O)_3](OTs)_2$ [62]. Thus cyclohexenone gave $[Ru(\eta^6-phenol)_2]^{2+}$ as the main product. The tosylate may also coordinate through the arene ring, for example, the reaction of cyclopentenone afforded $[(\eta^6-tosylate)(\eta^6-hydroxycyclopentadienyl)Ru]^{2+}$ which was characterized by X-ray diffraction.

A stable, highly water soluble Ru-aqua-complex, containing 1,8-naphthyridine (napy) ligands, $[Ru_2(napy)_2(H_2O)_4Cl(OH)](ClO_4)_4$ was synthesized and characterized (X-ray structure). The complex serves as catalyst for the oxidation of several alcoholic substrates and for the epoxidation of *trans*- and *cis*-stilbene and cyclooctene [63].

4. Hydrogen activation, hydrogenation and hydrogen transfer reactions

Hydrogenation is one of the very first organometallic catalytic processes observed in aqueous solutions and continued to attract interest in 1995, as well. The results obtained prior to 1994 are summarized by Chaloner et al. [10]. Examples are also mentioned in the preceding chapter [42,44]. Perhaps the most obvious feature of the recent studies is the search for mechanistic clues to understand the changes in reaction rates and selectivities which often can be observed in comparison with analogous non-aqueous hydrogenation reactions. The development of new selective catalysts remained on the agenda, too.

In a systematic work on Rh- and Ru-hydrido clusters, $(\eta^6-C_6H_6)_2Ru_2Cl_4$ (**36**) was shown to react with hydrogen in aqueous solution [64]. Under mild conditions (1.5 atm H_2 , 20°C) and in the presence of $NaBF_4$ the tetrahydrido cluster, $[Ru_4(\eta^6-C_6H_6)_4H_4](BF_4)_2$ (**37**) was ob-

tained, while at 60 atm H_2 and 55°C the hexahydrido derivative, $[Ru_2(\eta^6-C_6H_6)H_6]Cl_2$ (**38**) formed. The latter is a catalyst for fumaric acid hydrogenation at 55 atm H_2 and 50°C in aqueous solution with a turnover frequency of 35 h^{-1} .

In the presence of Ag-carboxylates **36** reacts with H_2 giving the dinuclear $[Ru_2(\eta^6-C_6H_6)_2(\mu_2-OH)(\mu_2-H)(\mu_2-\eta^2-O_2CR)]^+$. When a mixture of **36** and $Cp^*Rh_2Cl_4$ was subjected to similar hydrogenation, one of the $(\eta^6-C_6H_6)Ru$ units was replaced by a Cp^*Rh moiety and the analogous bimetallic compound $[(\eta^6-C_6H_6)Ru(\mu_2-OH)(\mu_2-H)(\mu_2-\eta^2-O_2CR)Rh-Cp^*]^+$ could be isolated [65].

These and several related clusters have been structurally characterized by, among others, excessive use of X-ray diffraction.

The water soluble monobenzene complex of Ru^{II} , $[Ru(\eta^6-C_6H_6)(CH_3CN)_3](BF_4)_2$ (**39**) catalyzed the biphasic hydrogenation of olefins and α,β -unsaturated ketones with the retention of the catalyst in the aqueous phase [66]. However, during hydrogenation of benzaldehyde the ruthenium complex moved to the organic phase. With α,β -unsaturated ketones the catalyst is selective towards $C=C$ reduction; in fact, $C=O$ hydrogenation is negligible. In a benzene- D_2O system, $H-D$ exchange was observed between H_2 and D_2O . It was established that hydrogen activation takes place both on a monohydridic and a dihydridic pathway and the relative weight of the two catalytic cycles determines the yield and product distribution. In aqueous systems, heterolytic activation of H_2 is assisted by the strong solvation of H^+ and this is reflected by the solvent effects observed with **39** in the hydrogenation of benzylideneacetone (Table 2).

Formation of monohydrides was found a decisive factor in certain rhodium catalyzed hydrogenations in aqueous media. A detailed study [67] of hydrogenations in aqueous solutions was carried out with $RhCl(PTA)_3$. The complex is an active catalyst for reduction of olefinic and oxo-acids, as well as of allyl alcohol and sulfostyrene. Mechanistic investigations were done

Table 2

The effect of solvent on the hydrogenation of benzylideneacetone catalyzed by **39**

| Solvent (ml) | Product(s) | Yield (%) |
|----------------------|------------------------|-----------|
| CH_3CN (10) | 4-phenylbutan-2-one | 2 |
| CH_3CN/H_2O (10/2) | 4-phenylbutan-2-one | 15 |
| C_6H_6/H_2O (5/5) | 4-phenylbutan-2-one | 87 |
| | 1-phenylbut-1-ene-3-ol | 1 |
| | 4-phenylbutan-2-ol | 2 |

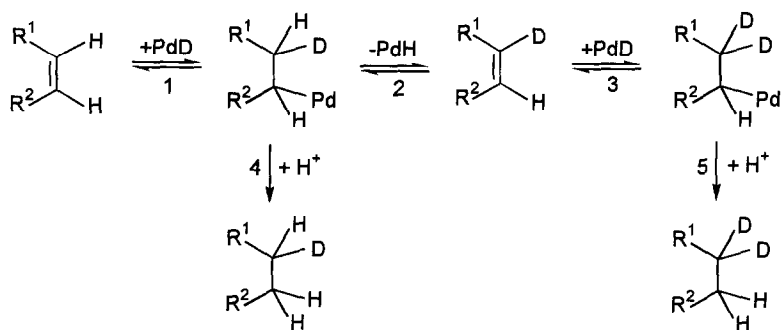
Conditions: $1.5-2.0 \times 10^{-5}$ mol catalyst; substrate/ $Ru = 10^3$; 40 atm H_2 ; 110°C; 4 h.

with crotonic acid and allyl alcohol substrates and, among other findings, showed pronounced maxima in the rates of hydrogenation of both substrates at pH 4.7. Hydrogenation of itaconic, crotonic and α -acetamidocinnamic acid in D_2O led to 45–100% deuteration of the products with 25–100% selectivity towards the α -carbon atom. These results, together with those of pH-static stoichiometric hydrogenation of $RhCl(PTA)_3$ suggest that the catalytically active species is $HRh(PTA)_3$ formed by dehydrochlorination of the primary product of H_2 oxidative addition. However, as shown by the incomplete deuteration of certain substrates, fully hydrogenated in D_2O , the dihydridic pathway may remain partially operative, similar to hydrogenations catalyzed by **39**.

$RhCl(PTA)_3$ is able to catalyze hydrogen transfer from aqueous formate to α,β -unsaturated aldehydes [68]. In contrast to the previously investigated $RuCl_2(PTA)_4$ catalyst [69], it showed marked selectivity towards the reduction of the $C=C$ bond. The catalyst could be recycled in the aqueous phase.

Reaction of unsaturated phospholipids, $R^1HC=CHR^2$, with D_2 in aqueous (H_2O) dispersions (liposomes), with Pd^{II} -alizarin red as catalyst, resulted in the formation of $R^1H_2C-CD_2R^2$ (in addition to the expected $R^1HDC-CDHR^2$) [70]. Conversely, only the symmetrically deuterated product was formed with H_2 in D_2O under otherwise identical conditions.

This finding could be explained by supposing the dominance of a monohydridic hydrogenation pathway and the reversible formation of an

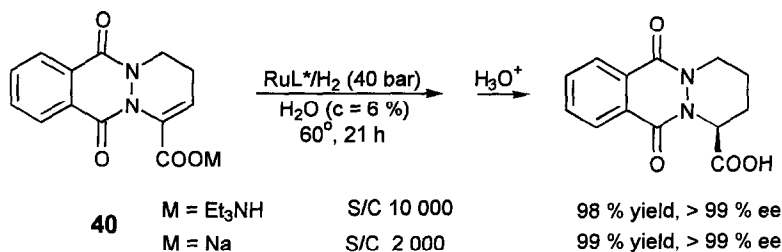


intermediate alkylpalladium species (steps 1 and 2 in Scheme 1).

Several Ru- and Rh-complexes of (*S*)-MeO-BIPHEP-TS-Na (**12**) were used [32] in hydrogenation of standard substrates such as α -acetamidocinnamic acid, Me- and Li- β -keto-butyrate, 2-oxo-propionate and 3,7-dimethyl-2,6-octadien-1-ol. In water, methanol and ethyl acetate–water solvents, at 20–25°C, under 10–60 atm H₂ high conversions (mostly in the 70–100% range) and high enantioselectivities (up to 98% enantiomeric excess, ee) could be achieved in 4–68 h reaction time. A ruthenium based catalyst was successfully applied for enantioselective hydrogenation of **40**, an intermediate for cilaprazil (Scheme 2).

Micellar effects play a considerable role in aqueous organometallic reactions. To further test this assumption the surface active diphosphine,

10 was synthesized on purpose and applied in the hydrogenation of methyl α -acetamidocinnamate, in combination with [RhCl(COD)]₂, both in homogeneous methanolic solutions and in ethyl acetate–water biphasic systems [33]. The results were compared to those obtained with the parent BDPP ligand. In homogeneous methanolic solution **10** gave nearly identical results as compared to BDPP and its tetrasulfonate (BDPPTS), i.e., 100% conversion in ≥ 1 h and 72–75% ee. However, in ethyl acetate–water mixtures the rhodium complex of the surfactant ligand showed considerably higher activity than that achieved with BDPTS while retaining enantioselectivity. Addition of Na₂HPO₄ decreased both the rate and selectivity. These results are in line with earlier findings in that phosphines which are capable of forming micelles can facilitate the catalytic re-



Scheme 2.

actions of lipophilic substrates in aqueous–organic biphasic reactions.

In a continuing study of the effect of surfactants on enantioselective hydrogenations [71,72] rhodium complexes of phosphinated glucopyranosides, such as $[\text{Rh}(\text{Me-}\alpha\text{-glup-OH})(\text{COD})]\text{BF}_4$ (**41**) and $[\text{Rh}(\text{Ph-}\beta\text{-glup-OH})(\text{COD})]\text{BF}_4$ (**42**) were used for hydrogenation of prochiral dehydroaminoacid derivatives in aqueous systems in the presence of sodium dodecyl sulfate (SDS) at 25°C and 1 atm H_2 . In most cases, addition of SDS increased both the rate and enantioselectivity of hydrogenations. In an extreme case, with **41** as catalyst, a 390 min reaction half time ($t_{1/2}$) was shortened to 6 min with a concomitant increase in the *S/R* ratio of the product from 11 (83.4% ee) to 68 (97.1% ee). Since to observe such effects the concentration of SDS had to exceed the critical micelle concentration, the changes in rates and selectivities could be attributed to true micellar effects. In a similar manner, solid polymeric surfactants (polysoaps, crosslinked polysoaps and amphiphilized ion exchangers, covalently or ionically modified with surfactants) were applied in the hydrogenation of *Z*-methyl-acetamidocinnamate catalyzed by $[(\text{BPPM})\text{Rh}(\text{COD})]\text{BF}_4$ (BPPM = (2*S*, 4*S*)-*N*-*t*-butoxycarbonyl-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine). Although both reaction rates and enantioselectivities were slightly lower with the immobilized catalysts than in the corresponding micellar solutions, the separation of the catalyst from the product was easy. The stability of the rhodium-containing amphiphilic ion exchanger catalyst was tested in recirculation experiments (9 cycles). Although the activity slowly decreased during these cycles there was no appreciable loss in enantioselectivity. It is noteworthy that high enantioselectivity was favored by micelle forming agents which are known to contain less water in their micellar core.

Hydrogenation of the water soluble $[\text{Ir}(\text{COD})(\text{PMe}_3)_3]\text{Cl}$ afforded the dihydride, *mer*- $\text{IrH}_2\text{Cl}(\text{PMe}_3)_3$ which showed stoichiometric addition reactions with alkynes and alkenes

and served as catalyst for the hydrogenation of these substrates in water. Water soluble amine complexes of the type $[\text{Ir}(\text{COD})(\text{en})]\text{Cl}$ (en = ethylenediamine) were found excellent precursors for aqueous hydrogenation catalysts [73].

In the complex obtained by the reaction of $[\text{Ru}(\text{H}_2\text{O})_6](\text{Ts})_2$ and *L* (= neocuproine (2,9-dimethyl-1,10-phenanthroline)), strong interaction between one of the tosylates and the Ru^{II} center was observed in the solid state (X-ray) so the product could be formulated as $[\text{Ru}(\text{H}_2\text{O})_6\text{L}_2(\text{Ts})](\text{Ts})$. With no added ligand, $[\text{Ru}(\text{H}_2\text{O})_6](\text{Ts})_2$ proved to be a catalyst of low activity for hydrogenation of unsaturated carboxylic acids in aqueous solutions (60°C, 1 atm total pressure) and for the reduction of aldehydes by hydrogen transfer from aqueous sodium formate [74].

$\text{Ru}_3(\text{CO})_{12}$ in combination with amines was found to reduce aromatic nitro compounds to the corresponding amines effectively [75], in partially aqueous solutions under 20–50 atm CO at 150–180°C. Turnover frequencies as high as 5.25×10^3 mol product (mol catalyst)⁻¹ h⁻¹ could be achieved in the reduction of nitrobenzene with triethylamine as the amine component and a diglyme/water 5/2 mixture as solvent. Since the reaction is highly selective for aromatic amines (ketones, nitriles, alkenes and alkynes do not react) and is accompanied by only negligible formation of gaseous H_2 it is speculated that it proceeds via an intramolecular hydrogen transfer in a hydrido–metal–nitrene intermediate without prior formation of H_2 in the water gas shift reaction.

5. Carbon–carbon bond formation

5.1. Hydroformylation

Progress in hydroformylation and carbonylation since 1980 has been very recently summarized and evaluated by leading experts both in research and production [13] and is dealt with in other chapters of this issue. Therefore, only a few selected examples are treated here.

A major improvement in both catalytic activity and selectivity of propene hydroformylation in the organic–aqueous biphasic system was achieved by using the newly synthesized BINAS-Na ligand (**5**) in combination with rhodium(III) acetate [76]. With considerably lower phosphorus/rhodium ratios than those typically used with TPPTS (6.8:1 in contrast to 80:1) stable systems were obtained with a catalytic activity as high as 178.5 (mol aldehydes) (mol Rh)⁻¹ min⁻¹, and an *n/iso* isomer ratio of butyric aldehyde 98:2. These data represent a twelve-fold increase in activity compared to what is obtained with TPPMS, with a further increase in selectivity. Keeping in mind that since the publication of the first reports on BINAS-Na [76,77] the preparation of analytically pure BINAS-8 has been worked out using orthoboric acid–sulfuric acid mixtures [22]. Exciting new developments can be expected concerning the mechanistic background of this exceptionally high activity and selectivity.

The search for catalysts of hydroformylation of higher olefins continued with varying success. Rh-complexes derived from tertiary 3- and 4-pyridylphosphines and from the newly synthesized ligands **16a–d** were shown comparable to HRh(CO)(PPh₃)₃ in hydroformylation of octene-1 in toluene (80°C, 20 atm syngas) [35]. Turnover frequencies around 35 mol aldehydes(mol rhodium)⁻¹ min⁻¹ were observed with most of the ligands but were as high as 70 with some of the pyridylphosphines. The *n/iso* ratio was 2.8 in all cases and was not effected by changes in the experimental parameters. Although the catalysts could be recycled by extraction into water at pH 1.5, the protonated complexes themselves did not show catalytic activity and therefore could not be used in a biphasic hydroformylation of octene-1.

Methyl esters of ω -alkenecarboxylic acids were subjected to hydroformylation in an aqueous biphasic system with Rh₄(CO)₁₂/TPPTS catalyst (*P/Rh* = 60) [78]. At 120°C and under 120 atm syngas methyl 4-pentenoate and 5-hexenoate could be hydroformylated with prac-

tically acceptable rate, however, esters of terminally unsaturated C₁₀, C₁₁ and C₁₄ carboxylic acids reacted slowly. Addition of tensides resulted in speeding up the reaction of the water insoluble higher olefinic acid derivatives but somewhat decreased the *n/iso* selectivity. For example, in the absence of surfactants methyl 9-decenoate gave methyl 11-formylundecanoate with 92/8 *n/iso* ratio; this was somewhat lower with anionic (86/14) and amphiphilic (80/20) and considerably lower with cationic tensides (70/30). On the other hand, the highest rates were observed with cationic tensides such as, e.g., octadecyltrimethylammonium bromide which could be attributed to the high local concentration of the negatively charged catalyst around the positively charged micellar surface, close to the substrate solubilized inside the micellar core. Most importantly, the catalyst could be retained in the aqueous phase and recycled after phase separation leaving no detectable amount of rhodium in the organic phase (> 1 ppm by X-ray fluorescence analysis).

Solubilization of higher olefins in the catalyst-containing aqueous phase could be achieved by using appropriately modified cyclodextrins [79] and this was reflected in increased hydroformylation rates. Thus, in the presence of dimethyl- β -cyclodextrin and a Rh/TPPTS catalyst, dec-1-ene reacted with 100% conversion, 95% selectivity to aldehydes and an *n/iso* ratio of 1.9 (*P* = 50 atm, CO/H₂ 1/1, 80°C). Particularly noteworthy is the high aldehyde selectivity which is attributed to the protective effect of complexation by the cyclodextrin host, which manifests itself in the drastically reduced rate of isomerization into internal decenes. After phase separation the organic phase contained > 0.5 ppm rhodium, that is the water soluble catalyst could be completely recovered in the aqueous phase.

Hanson and coworkers made a systematic study of salt effects in hydroformylation [80–82] both with the standard ligand, TPPTS and with the newly synthesized surfactant phosphines such as P[C₆H₄(CH₂)_{*x*}C₆H₄SO₃Na]₃, *x* = 3, 6.

It was shown by light scatter measurements that the new phosphines indeed formed aggregates in aqueous solutions in contrast to TPPTS which gave a true homogeneous solution. Octene-1 and hexene-1 were hydroformylated in aqueous–organic biphasic systems with $\text{Rh}(\text{acac})(\text{CO})_2$ as the catalyst precursor with Li_2SO_4 , Na_2SO_4 , Cs_2SO_4 , Na_2HPO_4 , and $\text{Al}_2(\text{SO}_4)_3$ as added salts. In case of the TPPMS-containing catalyst addition of salts decreased the rate of hydroformylation, however, in combination with the surface active phosphine a significant *increase* of the rate was observed. A decrease in rate upon increasing the ionic strength can be rationalized in a straightforward manner by taking into consideration the decreased solubility of all reactants. On the other hand, increasing the ionic strength results in pronounced aggregation of the catalyst with surfactant phosphines; the higher degree of solubilization of the substrate inside the micelles formed this way overcompensates the salting-out effect of salts. In addition, the catalyst substrate interaction is more favored by their relative proximity. Increased solubilization and close proximity result in increased hydroformylation rate.

Importantly, as shown by the above studies, addition of salts invariably increased the *n/iso* selectivity [80–82]. Hydroformylation of hexene-1 with $\text{HRh}(\text{CO})(\text{TPPTS})_3$ in water gave heptanals with an *n/iso* ratio of 4.4–5.1 (depending on conversion) which increased to 8.5 (Li_2SO_4), 8.0 (Na_2SO_4) and 10.4 (Cs_2SO_4). It is very likely, that the role of these ‘spectator cations’ is in the stabilization of $\text{HRh}(\text{CO})(\text{TPPTS})_2$ against further dissociation by participating in a highly organized network of anion–ca-

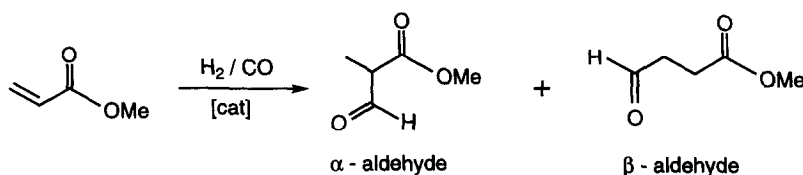
tion interaction and hydrogen bonding [54,55] around the negatively charged outer sphere of the rhodium complex.

Further attempts were made to apply the oxo-reaction for the synthesis of fine chemicals. As an example, styrene could be efficiently hydroformylated [29] with a Rh^I complex of the surfactant phosphine **10**. Although the catalyst is chiral, no optical induction was observed which is in line with the known poor enantioselectivity of complexes with monodentate chiral phosphines.

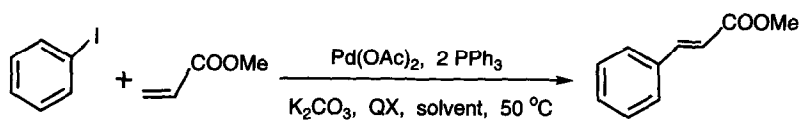
Hydroformylation of methyl acrylate (Scheme 3) to α -branched aldehyde is a useful reaction providing chiral building blocks after enzymatic hydrogenation.

This reaction was studied using rhodium catalysts prepared from $\text{Rh}(\text{acac})(\text{CO})_2$ and the new phosphines **17** and **18** and with TPPMS in various solvents (water, toluene, THF, water–toluene) at 50–80°C, with 10–50 atm syngas [36]. Under optimal conditions the aldehydes were obtained in high yield (80%) and with the desired selectivity (α/β ratio 20:1). In contrast to TPPMS in which case some of the rhodium moved to the organic phase complexes with **17** and **18** were withheld exclusively in the aqueous phase when a water–toluene mixture was used.

Even faster and more selective hydroformylation of methyl acrylate was observed [83] under similar conditions in biphasic systems with PPh_3 , TPPTS, 1,4-bis(diphenylphosphino)butane, DPPB, and its tetrasulfonate, DPPBTS in combination with $\text{Rh}(\text{acac})(\text{CO})_2$; the α/β ratio of aldehydes was generally > 100 , in a few cases > 200 . Even more surprising is the unprecedented observation that immobilizing the



Scheme 3.



Scheme 4.

Rh/TPPTS catalyst on wet SiO_2 yielded an extremely active supported aqueous phase (SAP) catalyst the activity of which much surpassed that of a comparable homogeneous or biphasic systems. The catalytic activity of such SAP catalysts depended largely on the water content of the SiO_2 support, a sharp maximum being observed for 37% by weight. Under such optimum conditions an initial turnover frequency of 4300 h^{-1} was observed in contrast to the value of 545 h^{-1} in a water–toluene biphasic system. Very likely this is not a general phenomenon, since similar hydroformylation experiments with propylene, a non-polar substrate, did not show increased rates on transposition from biphasic to SAP conditions. It is hypothesized that polar interactions of methyl acrylate with the hydrated silica gel is responsible for this unusual finding.

Engineering aspects of hydroformylation of octene-1 using a Rh/TPPMS catalyst were discussed [84]. In search for new methods of catalyst heterogenization in immiscible liquid phases an alternative [85] to the fluoruous biphasic method [86] has been suggested.

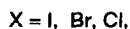
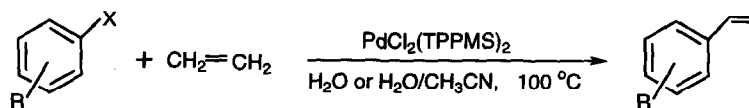
5.2. Other reactions with carbon–carbon bond formation

This period has been characterized by the more and more diverse application of aqueous

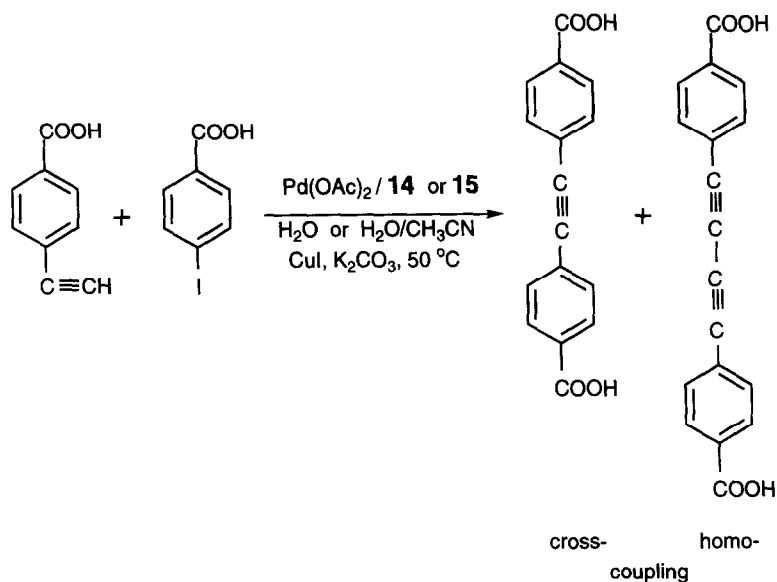
organometallic chemistry for the synthesis of fine chemicals. Several methods have been developed using partially or completely aqueous solutions and aqueous–organic biphasic systems for realization of useful transformations known from the armoury of classical ‘non-aqueous’ organic chemistry. Although some of these methods allow recirculation of the transition metal catalyst in the aqueous phase, this was usually of secondary importance in working out laboratory scale procedures.

The palladium(II)-catalyzed reaction of haloarenes with alkenes or alkynes (*Heck-type reactions*) is an extremely useful synthetic method and several variations to perform the reaction in aqueous media became known in the last few years. Both inter- and intramolecular [87] couplings have been studied. The catalyst is usually prepared in situ from Pd(OAc)_2 and a tertiary phosphine and the reaction requires the presence of a base, such as K_2CO_3 . It is also known that addition of CuI accelerates the process and quaternary ammonium salts (QX) can also have beneficial effect on the reaction.

When iodobenzene was reacted with methyl acrylate (Scheme 4) under the catalytic influence of $\text{Pd(OAc)}_2 + 2 \text{ PPh}_3$ in dry CH_3CN the addition of anhydrous $n\text{-Bu}_4\text{NCl}$ did not have an accelerating effect (10% yield as compared to 15% in the absence of QX). However, when



Scheme 5.



Scheme 6.

hydrated $n\text{-Bu}_4\text{NCl}$ was used 99% yield of methyl cinnamate was obtained [88].

Extension of this observation to the use of water– CH_3CN mixtures resulted in almost quantitative yields not only with $n\text{-Bu}_4\text{NCl}$, but with $n\text{-Bu}_4\text{NHSO}_4$, too, the latter usually being considered as inferior to bromides or chlorides. The reaction could be effected even without an organic solvent, in a mixture of the organic phase of the reactants and water.

The Heck arylation of ethylene in aqueous systems could be severely effected by Wacker-type side reactions. It was found, however, that iodoarenes (except 4-iodoaniline) reacted cleanly with ethylene (Scheme 5) using a *preformed* $\text{PdCl}_2(\text{TPPMS})_2$ catalyst at 100°C and 20–50

atm ethylene pressure [89]. The yield of the product styrenes was in the 60–100% range.

In situ mixing of $\text{Pd}(\text{OAc})_2 + 2 \text{ TPPMS}$ was much less effective. Interestingly, 4-iodophenol reaction gave exclusively 1-(4-hydroxyphenyl)ethanol (77% yield) which is the hydration product of 4-hydroxystyrene.

High purity *o*- and *p*-vinyltoluenes were prepared on a large scale by the Heck-arylation of bromotoluenes in a dimethylformamide–water mixture. The aqueous solvent allowed the use of an inorganic base (K_2CO_3) instead of triethylamine [90].

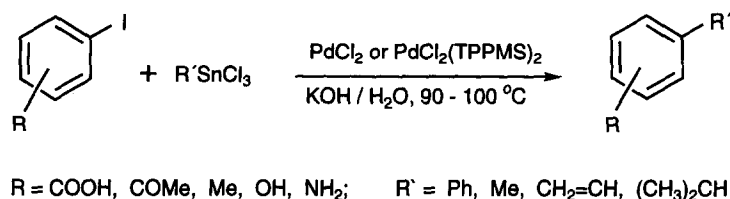
The guanidino phosphines **14** and **15** were tested in the reaction of 4-iodobenzoic acid and 4-carboxyphenylacetylene (Scheme 6) in combi-

Table 3
Comparison of Pd complexes with TPPTS (**3**) and the guanidino phosphines **14** and **15** as catalysts in Heck-coupling (Scheme 6).

| Solvent | | H_2O | | $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (1/1) | | |
|-----------|----------|----------------------|------------|---|-----------|------------|
| Phosphine | time (h) | conv. (%) | cross/homo | time (h) | conv. (%) | cross/homo |
| 3 | < 3 | 100 | ∞ | 0.3 | 100 | ∞ |
| 14 | 3 | 33 | 1/1.5 | 0.3 | 30 | 2/1 |
| 15 | 1 | 60 | 1/1 | 0.3 | 30 | 1/3 |

Conditions: 5 mol% $\text{Pd}(\text{OAc})_2$, $\text{P}/\text{Pd} = 5$, 10 mol% CuI , 50°C .

Selectivity is expressed as the HPLC peak height ($\lambda = 254 \text{ nm}$) of the products of homo- and cross-coupling.



Scheme 7.

nation with $\text{Pd}(\text{OAc})_2$ and CuI both in water and in water/acetonitrile 1/1 as solvent [34].

The results were compared to those obtained with TPPTS. It is seen from the data in Table 3, that palladium complexes of the new phosphines were somewhat less effective and markedly less selective in homo- versus cross-coupling than that formed from $\text{Pd}(\text{OAc})_2$ and TPPTS.

The reaction of water soluble aryl and vinyl halides with allyl-, aryl- and vinyltrichlorostannanes (*Stille-coupling*) in 1 M aqueous KOH solution was efficiently catalyzed by a catalyst prepared in situ from $\text{PdCl}_2 + 2 \text{ TPPMS}$ (Scheme 7) [91].

The yields are generally good to excellent. In a parallel study [92] TPPDS was used as the phosphine component ($\text{P/Pd} = 4$) with equally good results. This is a rare example of application of the disulfonated triphenylphosphine in catalysis.

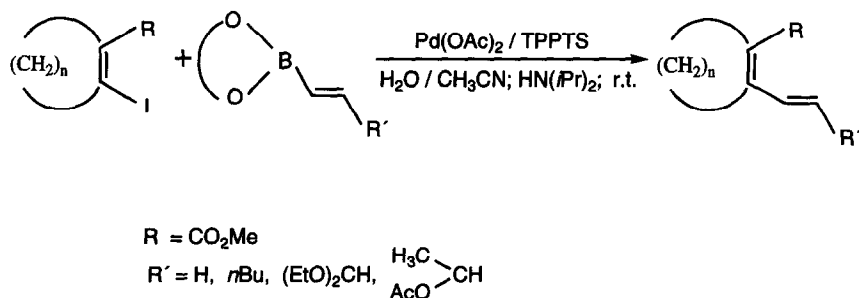
The *Suzuki-type cross coupling* catalyzed by $\text{Pd}(\text{OAc})_2/\text{TPPTS}$ in aqueous solutions (Scheme 8) can be carried out under very mild conditions [93] and the water soluble catalyst

can also be removed cleanly. In general, the yields are good to excellent.

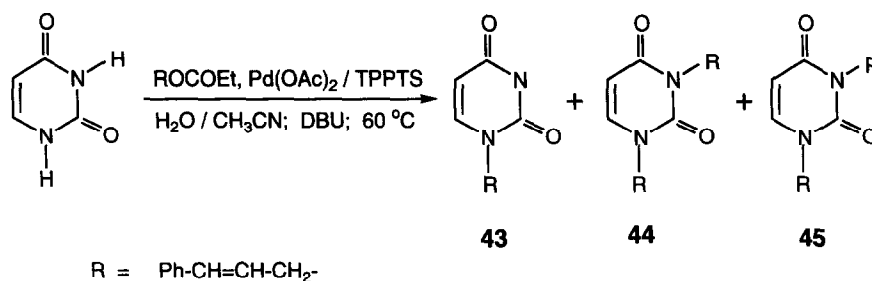
Owing to the mild conditions the coupling proceeds with retention of *Z*-olefin geometry. Vinyl boronic esters containing an allyl acetate or acetal moiety are also coupled with 3-iodoacrylate with acceptable yield (60–70%).

Reaction of both carbon- and heteronucleophiles with several allylic substrates [94] is catalyzed by $\text{Pd}(\text{OAc})_2/\text{TPPTS}$ in mixtures of water and a nitrile under very mild conditions with excellent yields and selectivity, both in homogeneous solution ($\text{CH}_3\text{CN-H}_2\text{O}$) and in biphasic systems (e.g., benzonitrile- H_2O). In the latter case, the catalyst could be recycled in the aqueous phase with practically no loss of activity and selectivity. Tetrasulfonated 1,2-bis(diphenylphosphino)ethane (**8**), and 1,4-bis(diphenylphosphino)butane were also used but did not offer advantages over the use of TPPTS.

Investigation of the palladium catalyzed *allylation* [95] of uracils and 2-thiouracils have shown that highly regioselective reactions can be achieved in aqueous media in contrast to the



Scheme 8.



Scheme 9.

conventional method using DMSO. As an example, Pd(OAc)₂–TPPTS catalyzed reaction of uracil with cinnamyl acetate in water–acetonitrile afforded selectively 1-cinnamyluracil (**43**), in high yield (Scheme 9), whereas a mixture of *N*-allylation products, **43**–**45**, was obtained with cinnamyl ethyl carbonate and Pd(PPh₃)₄ in DMSO.

Selective and productive *telomerization* of butadiene with water under palladium catalysis continues to be a challenge and is investigated in several laboratories.

It has been shown recently [96] that in the presence of certain amines and CO₂ the in situ catalyst, formed in aqueous solution from Pd(OAc)₂ and sulfonated phosphines (**1** and **3**) efficiently promoted the *telomerization* of 1,3-butadiene with water to yield 2,7-octadien-1-ol with *no added organic solvent* (Scheme 10).

Turnover frequencies as high as 269 mol converted butadiene per h per mol Pd were achieved. The amine structure had a decisive influence on the rate and selectivity. Only those amines, having one long alkyl chain, exemplified by dimethyldodecylamine, were found suitable additives. It seems plausible that the reaction of such amines with CO₂ and water converts them into cationic surfactants capable of

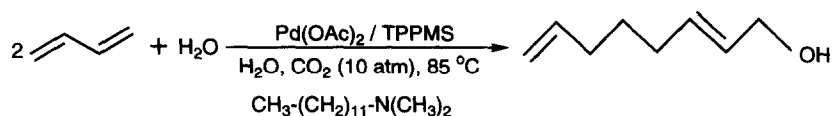
micelle formation and the telomerization actually takes place in a micellar environment.

In a partially aqueous system Pd(acac)₂ + 5 PPh₃ or 12 P(*o*-tolyl)₃ catalyzed the novel *cyclodimerization* [97] of 1,3-butadiene to 2-vinylmethylenecyclopentane (Scheme 11) in the presence of carbon dioxide.

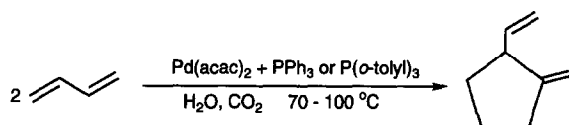
Although palladium is usually ineffective in such cyclodimerization reactions, the cyclopentane derivative could be made the major product at elevated temperatures (max. 87% selectivity). At lower temperatures the products of telomerization with water, 2,7-octadien-1-ol and 1,7-octadien-3-ol were formed preferentially.

Following their earlier success with RuCl₃ · aq. and [Ru(H₂O)₆]²⁺ catalysts for the ring opening metathesis polymerization (ROMP) of cyclic olefins, Grubbs and coworkers have shown that a water stable Ru-carbene, derived from RuCl₂(PPh₃)₄ and diphenylcyclopropene was an outstandingly effective catalyst for the ROMP of strained olefins bearing a variety of functional groups (Scheme 12). The catalyst gave living polymers and allowed the synthesis of various block polymers.

Replacement of PPh₃ by TPPTS provided a water soluble variant of this polymerization catalyst (Scheme 12) with retaining its activity for



Scheme 10.



the polymerization of water-soluble monomers [98].

Aqueous ROMP of carbohydrate-bearing 7-oxanorbornene derivatives [99] with $\text{RuCl}_3 \cdot \text{aq}$ as catalyst proved a method of choice for the preparation of a carbohydrate functionalized polymer which blocked protein-initiated cell agglutination efficiently.

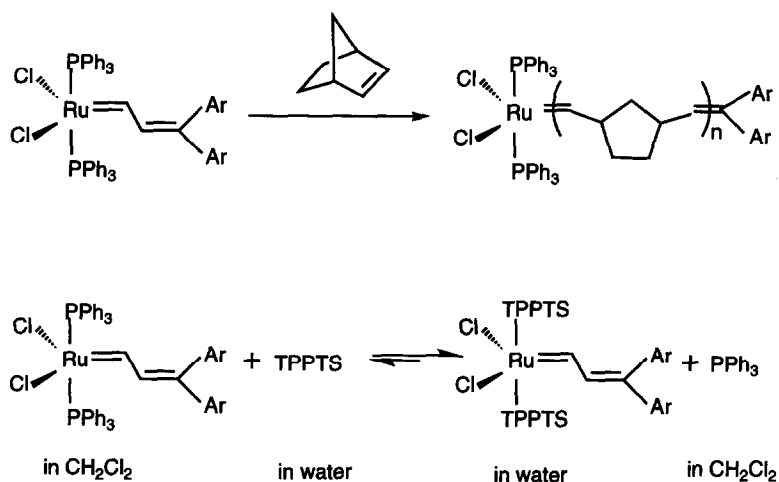
The strictly alternating copolymerization of ethylene and carbon monoxide and the terpolymerization of ethylene, propylene and CO was catalyzed by the Pd-complex of sulfonated 1,3-bis(diphenylphosphino)propane, **9** [28]. $[\text{Pd}(\mathbf{9})(\text{H}_2\text{O})_2](\text{BF}_4)_2$ was prepared by reacting $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ and **9** in neat water and the copolymerization was run with no addition of other solvents. Although, as judged by the structural analysis of the copolymers formed, the catalyst showed the same reactivity as its water insoluble analog, $[\text{Pd}(\text{dppp})(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ in a

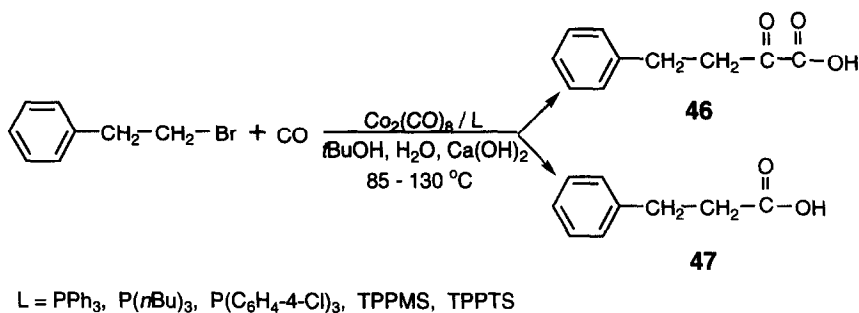
$\text{MeNO}_2/\text{MeOH}$ 2/1 solvent, the productivity was much lower in the aqueous system: 470 g copolymer/g Pd instead of 28 kg copolymer/g Pd. This is most probably due to the low solubility of the reactant gases in the catalyst-containing aqueous phase.

Oligomerization of olefins in water could be catalyzed by *mer*- $\text{IrHCl}_2(\text{PMe}_3)_3$ which was prepared by the protonation of the readily available *mer*- $\text{IrH}_2\text{Cl}(\text{PMe}_3)_3$ [73].

Among the carbonylation reactions, it was shown that addition of phosphines to the $\text{Co}_2(\text{CO})_8$ -catalyzed carbonylation of phenethyl bromide in a partly aqueous system (Scheme 13) changed its course dramatically [100]. $\text{Co}_2(\text{CO})_8$ alone led to the formation of the products of double and monocarbonylation, benzylpyruvic acid (**46**), and benzylacetic acid (**47**), respectively, in a ratio of 7.3. Hydrophobic phosphines, such as PPh_3 , $\text{P}(\text{n-Bu})_3$, etc. almost completely inhibited carbonylation and only phenethyl alcohol, styrene and ethylbenzene, together with coupling products could be obtained.

On the other hand, with addition of TPPTS or with pre-formed $\text{Co}_2(\text{CO})_6(\text{TPPTS})_2$, carbonylation proceeded with the same rate as with the non-modified $\text{Co}_2(\text{CO})_8$ catalyst; however, the





Scheme 13.

selectivity decreased significantly (**46/47** = 2.0–2.1). Co₂(CO)₆(TPPMS)₂ proved less active but, interestingly, showed an opposite selectivity (**46/47** = 0.3).

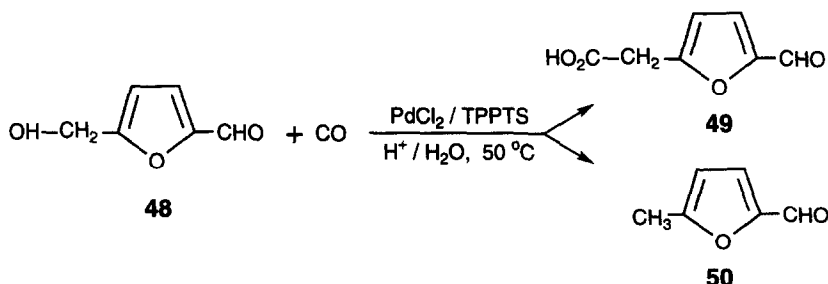
Carbonylation of bromobenzene with Pd (TPPTS)₃ in a toluene–water biphasic system yielded benzoic acid exclusively. Attempted reductive carbonylation either with H₂/CO or with HCOONa/CO failed to produce any benzaldehyde [101].

The same catalyst, prepared in situ from PdCl₂ and TPPTS catalyzed the carbonylation of 5-hydroxymethylfurfural (**48**) in acidic aqueous solution to 5-formylfuran-2-acetic acid (**49**) [102]. The only byproduct was 5-methylfurfural (**50**), resulting from the reduction of **48** (Scheme 14).

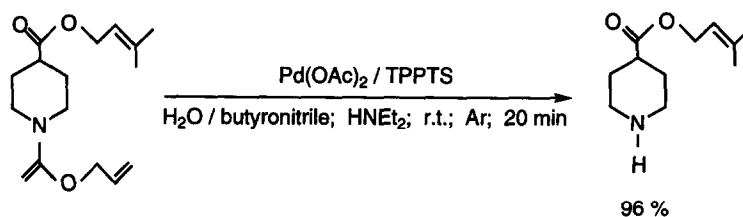
Increasing the P/Pd ratio (up to 12) decreased the reaction rate but suppressed reduction, P/Pd = 6 being a good compromise. Non-coordinating acids (H₂SO₄, H₃PO₄, etc.) gave the same result, however, the **49:50** ratio

changed dramatically by changing X in HX used as the acid component (HCl 71:29; HBr 48:52; HI 0:100). These are remarkable discoveries for at least three reasons. First, the starting material **48** is readily obtained from hydrocarbon sources (i.e., on a renewable basis) and the carbonylation product **49** is a precursor to 2,5-furandiacetic acid, a valuable raw material for polyesters and polyamides. Second, the solubility properties of hydrocarbons and derivatives prefer or require aqueous solutions for their reactions, which on the other hand has environmental benefits. Finally, the selective reduction of the hydroxymethyl functionality to a methyl in the presence of HI is very rare example of homogeneously catalyzed deoxygenation.

Superheated and supercritical water is widely known as an excellent medium for *destruction* of organic compounds. Successful efforts were made recently to use this unique solvent, which dissolves non-polar organic compounds, for *synthesis*, using, for example, Heck-coupling



Scheme 14.



Scheme 15.

[103] and metal catalyzed Diels–Alder reactions [104].

6. Other reactions

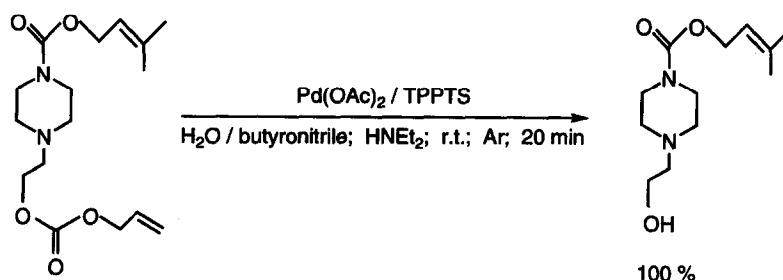
The mechanism of olefin *isomerization* catalyzed by $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ was extensively studied both with non-functionalized [105] and with functionalized [106] olefins (the latter involving allylic ethers and alcohols). By use of specifically deuterated substrates (such as 3-phenylpropene-3,3- d_2 and allyl-1,1- d_2 alcohol), deuterium crossover experiments and carrying out the reaction in D_2O the mechanism could be clearly identified as an intermolecular one, i.e., olefin isomerization proceeds through an addition–elimination mechanism with a metal hydride catalytic species. Directing effects of the functional groups have also been observed.

Isomerization of allylbenzene was studied to test the catalytic performance of sol gel entrapped $\text{trans-IrCl}(\text{CO})(\text{PPh}_3)_2$, $\text{RhCl}(\text{PPh}_3)_3$, $\text{RuCl}_2(\text{PPh}_3)_3$ and their water soluble analogs, $\text{trans-IrCl}(\text{CO})(\text{TPPMS})_2$, $\text{RhCl}(\text{TPPMS})_3$ and

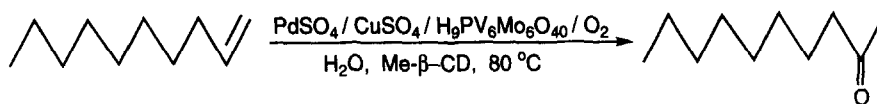
$\text{RuCl}_2(\text{TPPMS})_2$, the last heterogenized complex being the most active catalyst [46]. Water solubility of the complexes facilitated the immobilization in the aqueous reaction mixture used for the preparation of sol gel glasses. The same reaction was studied with a $\text{RhCl}(\text{PTA})_3$ catalyst in aqueous organic biphasic systems [68]. Efficient isomerization required presence of HCOONa which also facilitated reduction; isomerization could be made the major process by using lower temperatures (e.g., 50°C).

The $\text{Pd}(\text{OAc})_2/\text{TPPTS}$ catalyst system is suitable for *removal of protective groups used in the π -allyl methodology* [107,108]. By careful choice of the amount of the catalyst and of the solvent system used (homogeneous $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solutions or biphasic butyronitrile–water mixtures) selective deprotection of allyloxycarbamates was achieved in the presence of a dimethylallyl carboxylate in the same molecule (Scheme 15).

Conversely, compounds, doubly protected as dimethylallyl carbamates and allyloxycarbonates could be selectively deprotected at the oxygen (Scheme 16).



Scheme 16.



Scheme 17.

Such perfect tuning of selectivity offers important new opportunities in fine chemical synthesis.

The *oxidation* of olefins to ketones in water, catalyzed by palladium–copper or palladium–heteropolyacid systems (Wacker process) is an important example of aqueous organometallic catalysis. Following earlier attempts [109,110], a highly efficient way of selective oxidation of olefins was discovered which applies PdSO_4 , CuSO_4 , $\text{H}_9\text{PV}_6\text{Mo}_6\text{O}_{40}$ and β -cyclodextrin derivatives as components of the catalytic mixture [111]. The best results were obtained with methylated β -cyclodextrin (Me- β -CD) which has high solubility both in water and in the organic phase (Scheme 17).

Ethylene *oxidation* by $[\text{PdCl}_3(\text{pyridine})]^-$ was studied in detail [112]. It was established that the hydroxypalladation adduct was much more stable towards decomposition to ethanal than the corresponding intermediate formed from $[\text{PdCl}_4]^{2-}$. As a direct consequence of the prolonged lifetime, CuCl_2 is able to intercept this intermediate to produce 2-chloroethanol. Indeed, with $[\text{PdCl}_3(\text{pyridine})]^-$, $[\text{CuCl}_2] = 8$ M and $[\text{Cl}^-] = 0.2$ M the product was 98% 2-chloroethanol, while $[\text{PdCl}_4]^{2-}$ failed to produce appreciable amounts of 2-chloroethanol below chloride concentration of 3 M at any CuCl_2 concentration.

A genuine olefin *hydration*, the addition of

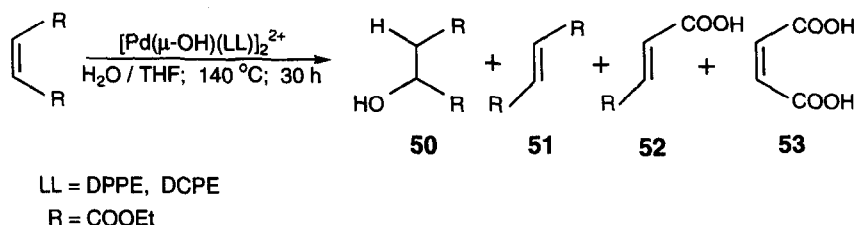
water to diethyl maleate to form diethyl malate (**50**) (Scheme 18) was achieved [38] in aqueous tetrahydrofuran solution with the complexes $[\text{Pd}(\mu\text{-OH})(\text{LL})_2]^{2+}$ as catalysts ($\text{LL} = 1,2$ -bis(diphenylphosphino)ethane, DPPE or 1,2-bis(dicyclohexylphosphino)ethane, DCPE). The reaction is accompanied by extensive hydrolysis and isomerization yielding **51–53**, but despite the low turnovers (approximately 3 mol of **50**/mol Pd) the reaction is truly catalytic and formation of an alcohol with a Pd/phosphine catalyst is a novel transformation. The same extent of hydration was observed with a mixture of $[\text{PdCl}_4]^{2-}$ and CuCl_2 , however, in that case the Wacker-type product, diethyl oxaloacetate was obtained, as well. Monodentate tertiary phosphines such as PPh_3 , $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SO}_3^-$ and **20** did not lead to appreciable hydration when used in combination with $[\text{PdCl}_4]^{2-}$.

Examples of aromatization of unsaturated cyclic ketones [62], oxidation of alcohols and epoxidation of stilbenes [63] are mentioned in Section 3.

Exhaustive recent reviews on aqueous organic chemistry are available [113,114].

Acknowledgements

This review has been written during a stay at the Department of Inorganic Chemistry, Univer-



Scheme 18.

sity of Zaragoza, Spain in the fall semester of 1995. We are grateful for the warm hospitality of Professor Luis A. Oro, his colleagues and students. The financial support by IBERDROLA S.A. of a visiting professorship (F.J.), as well as by the European Union (PECO Contract No. ERBCIPDCT940617) (Á.K.) is gratefully acknowledged. The Hungarian National Research Fund, OTKA is thanked for funding our research in this field (Grant No. 16697 to F.J.).

References

- [1] I.T. Horváth and F. Joó, eds., NATO ASI Ser. 3 5 (1995).
- [2] 209th Meeting of the American Chemical Society, Anaheim, CA (1995) abstracts of papers.
- [3] F. Joó and Z. Tóth, *J. Mol. Catal.* 8 (1980) 369.
- [4] T.G. Southern, *Polyhedron* 8 (1989) 407.
- [5] D. Sinou, *Bull. Soc. Chim. Fr.* 3 (1987) 480.
- [6] E. Kuntz, *CHEMTECH* 17 (1987) 570.
- [7] M. Barton and J.D. Atwood, *J. Coord. Chem.* 24 (1991) 43.
- [8] P. Kalck and F. Monteil, *Adv. Organomet. Chem.* 34 (1992) 219.
- [9] W.A. Herrmann and C.W. Kohlpaintner, *Angew. Chem.* 105 (1993) 1588.
- [10] P.A. Chaloner, M.A. Esteruelas, F. Joó and L.A. Oro, *Homogeneous Hydrogenation (Catalysis by Metal Complexes, Vol. 15)* (Kluwer, Dordrecht, 1994).
- [11] D.M. Roundhill, *Adv. Organometal. Chem.* 38 (1995) 155.
- [12] B. Cornils and W.A. Herrmann, eds., *Applied Homogeneous Catalysis by Organometallic Complexes (VCH, Weinheim, 1996)*.
- [13] M. Beller, B. Cornils, C.D. Frohning and C.W. Kohlpaintner, *J. Mol. Catal. A* 104 (1995) 17.
- [14] B. Cornils and E. Wiebus, *CHEMTECH* 25 (1995) 33.
- [15] B. Cornils, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 1575.
- [16] B. Cornils and E.G. Kuntz, *J. Organometal. Chem.* 502 (1995) 177.
- [17] M.Y. Darensbourg, ed., *Inorg. Synth.* 32 (1996).
- [18] F. Joó and L. Vígh, In: eds. Y. Barenholz and D.D. Lasic, *Handbook of Nonmedical Applications of Liposomes, Vol. III: From Design to Microreactors* (CRC Press, Boca Raton, FL, 1996) p. 255.
- [19] U. Koelle, *Coord. Chem. Rev.* 135–136 (1994) 623.
- [20] G. Süß-Fink, A. Meister and G. Meister, *Coord. Chem. Rev.* 143 (1995) 97.
- [21] C. Mercier and P. Chabardes, *Pure Appl. Chem.* 66 (1994) 1509.
- [22] W.A. Herrmann, G.P. Albanese, R.B. Manetsberger, P. Lappe and H. Bahrmann, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 811.
- [23] O. Herd, K.P. Langhans, O. Stelzer, N. Weferling and W.S. Sheldrick, *Angew. Chem., Int. Ed. Engl.* 32 (1993) 1058.
- [24] O. Herd, A. Heßler, K.P. Langhans, O. Stelzer, W.S. Sheldrick and N. Weferling, *J. Organomet. Chem.* 475 (1994) 99.
- [25] F. Bitterer, S. Kucken and O. Stelzer, *Chem. Ber.* 128 (1995) 275.
- [26] A. Heßler, S. Kucken, O. Stelzer, J. Blotvogel-Baltronat and W.S. Sheldrick, *J. Organomet. Chem.* 501 (1995) 293.
- [27] T. Bartik, B. Bunn, B. Bartik and B.E. Hanson, *Inorg. Chem.* 33 (1994) 164.
- [28] Z. Jiang and A. Sen, *Macromolecules* 27 (1994) 7215.
- [29] T. Bartik, H. Ding, B. Bartik and B.E. Hanson, *J. Mol. Catal. A* 98 (1995) 117.
- [30] K. Heesche-Wagner and T. Mitchell, *J. Organometal. Chem.* 468 (1994) 99.
- [31] V. Ravindar, H. Hemling, H. Schumann and J. Blum, *Synth. Commun.* 22 (1992) 841.
- [32] E.A. Broger, R. Schmid, Y. Cramer, M. Lalonde, A. Meili and G. Schoettel, *Preprints NATO ARW on Aqueous Organometal. Chem. and Catal., Debrecen, Hungary* 29 Aug–1 Sept, 1994.
- [33] H. Ding, B.E. Hanson and J. Bakos, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 1645.
- [34] H. Dibowski and F.P. Schmidtchen, *Tetrahedron* 51 (1995) 2325.
- [35] A. Buhling, P.C.J. Kamer and P.W.N.M. van Leeuwen, *J. Mol. Catal. A* 98 (1995) 69.
- [36] G. Fremy, Y. Castanet, R. Grzybek, E. Monflier, A. Mortreux, A.M. Trzeciak and J.J. Ziolkowski, *J. Organometal. Chem.* 505 (1995) 11.
- [37] S. Ganguly, J.T. Mague and D.M. Roundhill, *Inorg. Chem.* 31 (1992) 3500.
- [38] S. Ganguly and D.M. Roundhill, *Organometallics* 12 (1993) 4825.
- [39] T.L. Schull, J.C. Fettinger and D.A. Knight, *J. Chem. Soc., Chem. Commun.* (1995) 1487.
- [40] B. Assmann, K. Angermaier and H. Schmidbauer, *J. Chem. Soc., Chem. Commun.* (1994) 941.
- [41] B. Assmann, K. Angermaier M. Paul, J. Riede and H. Schmidbauer, *Chem. Ber.* 128 (1995) 891.
- [42] F.P. Pruchnik, P. Smolenski and Y. Raksa, *Polish J. Chem.* 69 (1995) 5.
- [43] G. Papadogianakis, J.A. Peters, L. Maat and R.A. Sheldon, *J. Chem. Soc., Chem. Commun.* (1995) 1105.
- [44] A. Andriollo, A. Bolívar, F.A. Lopez and D.E. Paez, *Inorg. Chim. Acta* 238 (1995) 187.
- [45] A. Bényei and F. Joó, *J. Mol. Catal.* 58 (1990) 15; J.D. Atwood, P.J. Roman and R.L. Rominger, 209th Meet. of the Am. Chem. Soc., Anaheim, CA, INOR 413; F. Joó, L. Vígh, L. Nádasdi and É. Papp, 209th Meet. of the Am. Chem. Soc., Anaheim, CA, INOR 448.
- [46] H. Shertchook, D. Avnir, J. Blum, F. Joó, Á. Kathó, H. Schumann, R. Weimann and S. Wernik, *J. Mol. Catal. A*, 108 (1996) 153.
- [47] I.R. Baird, M.B. Smith and B.R. James, *Inorg. Chim. Acta* 235 (1995) 291.
- [48] I. Kovács and M.C. Baird, *J. Organometal. Chem.* 502 (1995) 87.

- [49] J.P. Fackler, Jr., R.J. Staples and Z. Assefa, *J. Chem. Soc. Chem. Commun.* (1994) 431.
- [50] Z. Assefa, B.G. McBurnett, R.J. Staples and J.P. Fackler, Jr., *Inorg. Chem.* 34 (1995) 75.
- [51] Z. Assefa, B.G. McBurnett, R.J. Staples and J.P. Fackler, Jr., *Inorg. Chem.* 34 (1995) 4965.
- [52] J.M. Forward, R.J. Staples and J.P. Fackler, Jr., *Organometallics* 14 (1995) 4194.
- [53] J.M. Forward, Z. Assefa and J.P. Fackler, Jr., *J. Am. Chem. Soc.* 117 (1995) 9103.
- [54] D.J. Darensbourg and C.J. Bischoff, *Inorg. Chem.* 32 (1993) 47.
- [55] I.T. Horváth, R. Kastrop, A. Oswald and E. Mozeleski, *Catal. Lett.* 2 (1989) 85.
- [56] M.S. Eisen, A. Haskel, H. Chen, N.M. Olmstead, D.P. Smith, M.F. Maestre and R.H. Fish, *Organometallics* 14 (1995) 2806.
- [57] H. Chen, N.M. Olmstead, D.P. Smith, M.F. Maestre and R.H. Fish, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 1514.
- [58] H. Chen, N.M. Olmstead, D.P. Smith, M.F. Maestre and R.H. Fish, *J. Am. Chem. Soc.* 117 (1995) 9097.
- [59] H. Chen, M.F. Maestre and R.H. Fish, *J. Am. Chem. Soc.* 117 (1995) 3631.
- [60] U. Kölle, R. Görissen and T. Wagner, *Chem. Ber.* 128 (1995) 911.
- [61] D. Carmona, F.J. Lahoz, R. Atencio, L.A. Oro, M. Pilar Lamata and E. San José, *Tetrahedron: Asymm.* 4 (1993) 1425.
- [62] U. Koelle, Chr. Weißschädel and U. Englert, *J. Organometal. Chem.* 490 (1995) 101.
- [63] A.E.M. Boehrijk, M.M. van Velzen, T.X. Neenan, J. Reedijk, H. Kooijman and A.L. Spek, *J. Chem. Soc., Chem. Commun.* (1995) 2465.
- [64] G. Meister, G. Rheinwald, H. Stoeckli-Evans and G. Süss-Fink, *J. Chem. Soc. Dalton Trans.* (1994) 3215.
- [65] G. Meister, G. Rheinwald, H. Stoeckli-Evans and G. Süss-Fink, *J. Organometal. Chem.* 496 (1995) 197.
- [66] W.-C. Chan, C.-P. Lau, L. Cheng and Y.-S. Leung, *J. Organometal. Chem.* 464 (1995) 103.
- [67] F. Joó, L. Nádasdi, A.Cs. Bényei and D.J. Darensbourg, *J. Organometal. Chem.*, 512 (1996) 45.
- [68] D.J. Darensbourg, N.W. Stafford, F. Joó and J.H. Reibenspies, *J. Organometal. Chem.* 488 (1995) 99.
- [69] D.J. Darensbourg, F. Joó, M. Kannisto, Á. Kathó and J.H. Reibenspies, *Inorg. Chem.* 33 (1994) 200.
- [70] B. Szalontai, F. Joó, É. Papp and L. Vigh, *J. Chem. Soc., Chem. Commun.* (1995) 2299.
- [71] A. Kumar, G. Oehme, J.P. Roque, M. Schwarze and R. Selke, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 2197.
- [72] H.N. Flach, Y. Grassert and G. Oehme, *Macromol. Chem. Phys.* 195 (1994) 3289.
- [73] J.S. Merola, M.A. Franks, P. Chirik and R. Pafford, 209th Meet. of the Am. Chem. Soc. Anaheim, CA, 1995, INOR 416.
- [74] a)A. C. Bényei, NATO ASI Ser. 3 5 (1995) 159; A.C. Bényei, S. Lehel, F. Joó, D.J. Darensbourg and J.H. Reibenspies, Abstracts of 9th ISHC, Jerusalem, 1994, p. 303.
- [75] K. Nomura, *J. Mol. Catal. A* 95 (1995) 203.
- [76] W.A. Herrmann, C.W. Kohlpaintner, R.B. Manetsberger, H. Bahrmann and H. Kottmann, *J. Mol. Catal. A* 97 (1995) 65.
- [77] W.A. Herrmann, G. Albanese, R. Manetsberger, R. Schmid and C. Schwer, NATO ASI Ser. 3 5 (1995) 127.
- [78] B. Fell, C. Schobben and G. Papadogianikis, *J. Mol. Catal. A* 101 (1995) 179.
- [79] E. Monflier, G. Fremy, Y. Castanet and A. Mortreux, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 2269.
- [80] H. Ding and B. Hanson, *J. Chem. Soc., Chem. Commun.* (1994) 2747.
- [81] H. Ding, B. Hanson and T.E. Glass, *Inorg. Chim. Acta* 229 (1995) 329.
- [82] H. Ding and B.E. Hanson, *J. Mol. Catal. A* 99 (1995) 131.
- [83] G. Fremy, E. Monflier, J.-F. Carpentier, Y. Castanet and A. Mortreux, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1474.
- [84] P. Purwanto and H. Delmas, *Catal. Today* 24 (1995) 135.
- [85] C. Bianchini, P. Frediani and V. Sernau, *Organometallics* 14 (1995) 5485.
- [86] I.T. Horváth and J. Rábai, *Science* 266 (1994) 72.
- [87] D.B. Grotjahn and X. Zhang, NATO ASI Ser. 3 5 (1995) 123.
- [88] T. Jeffery, *Tetrahedron Lett.* 35 (1994) 3051.
- [89] J. Kiji, T. Okano and T. Hasegawa, *J. Mol. Catal. A* 97 (1995) 73.
- [90] R.A. DeVries and A. Mendoza, *Organometallics* 13 (1994) 2405.
- [91] A.I. Roshchin, N.A. Bumagin and I.P. Beletskaya, *Tetrahedron Lett.* 36 (1995) 125.
- [92] R. Rai, K.B. Aubrecht and D.B. Collum, *Tetrahedron Lett.* 36 (1995) 3111.
- [93] J.P. Genêt, A. Linquist, E. Blart, V. Mouries, M. Savignac and M. Vaultier, *Tetrahedron Lett.* 36 (1995) 1443.
- [94] E. Blart, J.P. Genêt, M. Safi, M. Savignac and D. Sinou, *Tetrahedron* 50 (1994) 505.
- [95] S. Sigismondi, D. Sinou, M. Pérez, M. Moreno-Mañas, R. Pleixats and M. Villarroya, *Tetrahedron Lett.* 35 (1994) 7085.
- [96] E. Monflier, P. Bourdauducq, J.-L. Couturier, J. Kervennal and A. Mortreux, *J. Mol. Catal. A* 97 (1995) 29.
- [97] F. Bergamini, F. Panella, R. Santi and E. Antonelli, *J. Chem. Soc., Chem. Commun.* (1995) 931.
- [98] R.H. Grubbs, NATO ASI Ser. 3 5 (1995) 15.
- [99] K.H. Mortell, M. Gingras and L.L. Kiessling, *J. Am. Chem. Soc.* 116 (1994) 12053.
- [100] E. Monflier and A. Mortreux, *J. Mol. Catal.* 88 (1994) 295.
- [101] F. Monteil and P. Kalck, *J. Organometal. Chem.* 482 (1994) 45.
- [102] G. Papadogianakis, L. Maat and R.A. Sheldon, *J. Chem. Soc., Chem. Commun.* (1994) 2659.
- [103] E.J. Parsons, R.C. Crittendon, P. Daugherty, S. Metts and L.T. Keaise, 209th Meet. of the Am. Chem. Soc., Anaheim, CA, 1995, INOR 271.

- [104] R.L. Holliday, B.Y.M. Jong, M.B. Korzinski and J.W. Kolis, 209th Meet. of the Am. Chem. Soc., Anaheim, CA, 1995, INOR 268.
- [105] T. Karlen and A. Ludi, *J. Am. Chem. Soc.* 116 (1994) 11375
- [106] D.V. McGrath and R.H. Grubbs, *Organometallics* 13 (1994) 224.
- [107] S. Lemarie-Audoire, M. Savignac, E. Blart, G. Pourcelot and J.P. Genêt, *Tetrahedron Lett.* 35 (1994) 8783.
- [108] J.P. Genêt, E. Blart, M. Savignac, S. Lemeune, S. Lemarie-Audoire, J.-M. Paris and J.-M. Bernard, *Tetrahedron* 50 (1994) 497.
- [109] H.A. Zahalka, K. Januszkiewicz and H. Alper, *J. Mol. Catal.* 35 (1980) 249.
- [110] A. Harada, Y. Hu and S. Takahashi, *Chem. Lett.* (1986) 2083.
- [111] E. Monflier, E. Blouet, Y. Barbaux and A. Mortreux, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 2100.
- [112] J.W. Francis and P.M. Henry, *J. Mol. Catal. A* 99 (1995) 77.
- [113] C.-J. Li, *Chem. Rev.* 93 (1993) 2023.
- [114] A. Lubineau, J. Augé and Y. Queneau, *Synthesis* (1994) 741.