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Homogeneous catalysts based on water-soluble phosphines

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Contents

Abstract

Aryl- and alkyl-substituted tertiary phosphines are among the most common ligands used in homogeneous catalysts, but they are hydrophobic, as in general are the products of the catalysis. Therefore, there are two basic problems in homogeneous catalysis, namely the separation and subsequent recycling of the catalyst. These problems can be elegantly solved by using two-phase catalysis where, for example, the catalyst can be in a hydrophilic phase in which the organic products are insoluble. In order to transform homogeneous catalysts based on tertiary phosphines into water-soluble moieties, one approach is to make the phosphines water-soluble. Thus, when the catalytic reaction is complete, the products are in an organic phase and the catalyst is in the aqueous phase. Then, a simple phase separation enables the continuous re-use of the catalyst. However, if we compare biphasic reactions with their monophasic equivalents, we find that rates are lower in two-phase systems. This is mainly due to the fact that when the catalyst is in one phase and the substrates are in another, the interaction between the catalyst and the substrates is lower than in a monophasic system, thus reducing the rate of the reactions. A way to remove disadvantages of both monophasic and biphasic catalysis is to introduce ligands that confer a thermoregulated phase-transfer function to the catalyst. The strategy of the thermoregulated phase-transfer catalysis (TRPTC) is that before the reaction, the catalyst resides in the aqueous phase and the substrates in the organic phase as in regular biphasic catalysis, but at higher temperature the catalyst can transfer into the organic phase to catalyse the reaction, as in a homogeneous system, and then return to the aqueous phase to be separated from the product at lower temperature.

Keywords: Homogeneous catalysts; Water-soluble phosphines; Aqueous phase

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1. Water-soluble phosphines

The main disadvantage of homogeneous catalysis is the difficulty associated with separating the catalyst from the product and solvent. Separation techniques, such as distillation, require a lot of energy and can lead to degradation of both the product and catalyst used. A possible solution to these problems is to separate the catalyst and the product into two individual and immiscible phases. Reactions may then be performed as shown in Fig. 1.

Before the reaction (a), the catalyst resides in the aqueous phase with the substrates being in the organic phase. During the reaction (b), the two layers are vigorously stirred, thus allowing suitable interaction of the catalyst and the substrates. Once the reaction is finished (c), the stirring is stopped and the mixture separates into two layers, one containing the product and the other the catalyst. Separation of the two phases is then carried out by simple decantation and the catalyst solution is available for immediate re-use.

This type of approach was first used commercially with a nickel complex for the polymerisation of ethylene: the Shell Higher Olefin Process (SHOP) [1]. In this case, the catalyst and substrate are in a single phase and the product forms a second, immiscible phase. However, the principle is the same.

This approach is, unfortunately, not suitable for many reactions and water is preferred as a catalyst solvent for biphasic conditions. The selection of water as a second phase offers many benefits: water is a cheap and environmentally friendly solvent; moreover there are a wide range of organic solvents which are immiscible with water.

One class of ligands widely used in homogeneous catalysis is phosphines. Inducing hydrophilicity into a phosphine can be achieved by introducing polar groups, [2] such as:

Sulfonated groups	$-SO_3H$, $-SO_3^-Na^+$
Ammonium groups	$-NR_3^+$, NR_3
Carboxylate groups	$-COOH$, $-COO^-Na^+$
Carbohydrate groups	$-C_5H_{9-n}O(OH)_n$
Phosphonium and phosphonate groups	$-PR_3^+$, $-P(O)(OR)_2$, $-P(O)(ONa)_2$
Hydroxyalkyl and polyether groups	$-OH$, $-(CH_2CH_2O)_n-H$

Examples of these phosphines are shown below and their activity in catalysis described. For some of the most classical catalytic reactions in which the phosphines are tested as ligands—the hydroformylation of 1-octene and 1-hexene or the hydrogenation of styrene and 1-hexene—the reaction conditions for the different phosphines are collected in tables so that a comparison of their efficiency is possible.

1.1. Phosphines containing sulfonated groups

In many cases, water-soluble transition metal catalysts are prepared with sulfonated phosphine ligands. The most widely used are (3-sulfonatophenyl)diphenylphosphine (TPPMS) and tris(3-sulfonatophenyl)phosphine (TPPTS) (Fig. 2); in general, both are used as their sodium salts and their solubilities in water are, respectively, 80 g dm^{-3} and 1100 g dm^{-3} [3].

The monosulfonated triphenylphosphine, TPPMS, was first synthesised in 1958 by Ahrland et al. [4]; it is used as a ligand for the selective hydrogenation of cinnamaldehyde by hydrogen transfer (from aqueous

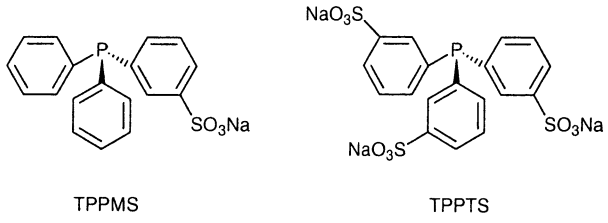


Fig. 2. The phosphines TPPMS and TPPTS.

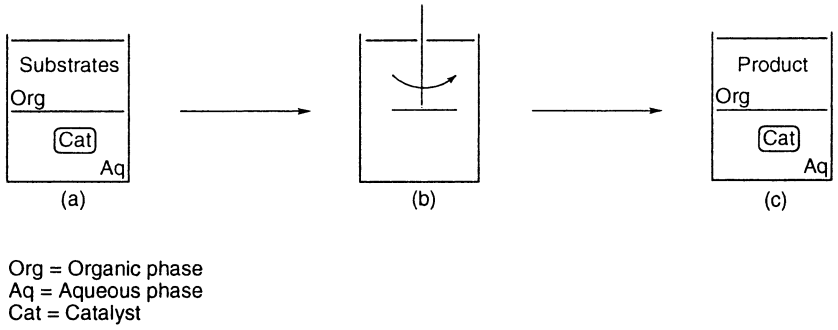
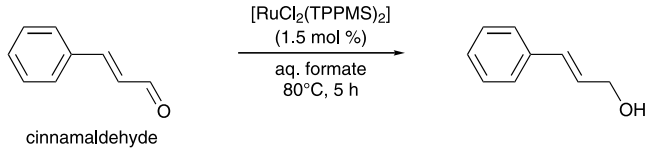


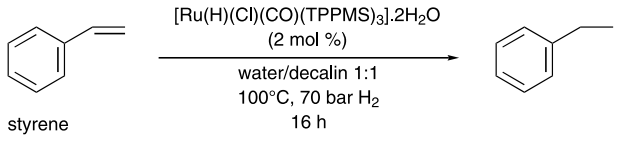
Fig. 1. Process of biphasic catalytic reactions, (a) before the reaction, (b) emulsion formed by stirring during the reaction and (c) at the end of the reaction.

formate) with $[RuCl_2(TPPMS)_2]$ to give the corresponding unsaturated alcohol in 98% yield (Eq. (1)) [5].



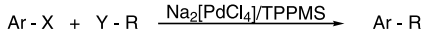
(1)

The pre-formed complex $[Ru(H)(Cl)(CO)(TPPMS)_3]\cdot 2H_2O$ shows catalytic activity for the hydrogenation of styrene (Eq. (2)) and cyclohexene [6]. In water/decalin, with a substrate/catalyst ratio of 50:1, styrene is hydrogenated to ethybenzene with a conversion of 86% and an activity [(mol substrate consumed) (mol catalyst)$^{-1}$ (h)$^{-1}$] of 3 h^{-1}. Under the same conditions, cyclohexene is transformed into cyclohexane in 25% yield, with an activity of 1.1 h^{-1}.



(2)

The cross-coupling reaction is another catalytic application that can involve TPPMS as a ligand, for example in the alkylation of organic substrates in water/acetonitrile mixtures (Eq. (3)) [7]. The coupling reaction of aryl and vinyl boronic acids with both hydrophilic and hydrophobic organic halides (Eq. (3)-(a)) is complete within several hours (3–10 h) in the presence of 5–15 mol.% of $[Pd(TPPMS)_3]$ in a basic aqueous phase or a basic two-phase system at 80 °C, and the yields of the coupled products range from moderate to excellent (70–98%). The alkylation of aryl and heteroaromatic halides by terminal alkynes is also catalysed by $[Pd(TPPMS)_3]$ (Eq. (3)-(b)). With $[Pd(TPPMS)_3]$ (10 mol.%) and a CuI promoter, in water/acetonitrile (1:1) at room temperature, a complete conversion of the organic iodides occurs and the yields range from 65 to 100%.

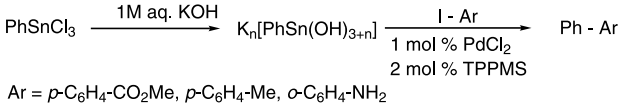


(a) Ar = *p*-C_6H_4-CH_3, 4-C_5H_4N, *p*-C_6H_4-CH_2CO_2H, *p*-$C_6H_4SO_3Na$
X = I, Br
R = -C_6H_5, -C_6H_4-*p*-CH_3, -(*E*)-CH=CH-C_6H_5
Y = -$B(OH)_2$

(b) Ar = *p*-I-C_6H_4-
X = I
R = -$COOCH_2CH_3$, -C_6H_5
Y = HC≡C-

(3)

The cross-coupling of tin halide compounds and aryl iodides in aqueous alkaline solution gives, with $PdCl_2/(TPPMS)_2$, the coupled phenyl–aryl product in ca. 85% yield (Eq. (4)) [8].



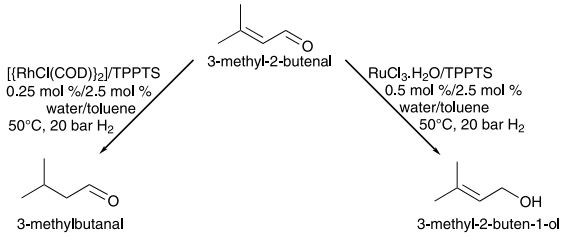
(4)

Some water-soluble iridium–TPPMS complexes have been recently synthesised but no catalytic studies have yet been reported [9].

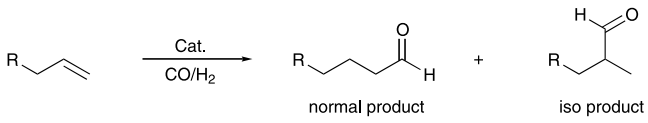
The use of trisulfonated triphenylphosphine, TPPTS, as a ligand has also been widely reviewed. It is present in water-soluble complexes with various metals such as manganese, iron, ruthenium, cobalt, rhodium, iridium, nickel, palladium, platinum, silver or gold [10].

With a ruthenium precursor and TPPTS, α,β-unsaturated aldehydes are selectively reduced to the corresponding α,β-unsaturated alcohols, whereas with a rhodium precursor and TPPTS, α,β-unsaturated aldehydes are hydrogenated to the corresponding saturated aldehydes [11]. For example, as shown in the Scheme 1, in the presence of $RuCl_3\cdot H_2O$/TPPTS in water/toluene, the α,β-unsaturated aldehyde 3-methyl-2-butenal (prenal) is reduced with a total conversion and the corresponding α,β-unsaturated alcohol, 3-methyl-2-buten-1-ol (prenol), is obtained with the very good selectivity of 96%. The same compound, 3-methyl-2-butenal is reduced by $[\{RhCl(COD)\}_2]$/TPPTS (COD = 1,5-cyclooctadiene) in 90% yield and gives the corresponding saturated aldehyde, 3-methylbutanal, with a selectivity of 95%.

The phosphine, TPPTS, is also efficient as a ligand in transition metal complexes for the hydroformylation reactions in water/organic systems. Hydroformylation reactions occur in the presence of carbon monoxide and hydrogen and the primary product is an aldehyde containing one more carbon atom than the alkene substrate. Two possible aldehyde products are formed from an unsymmetrical alkene substrate, they are referred to as the 'normal' and the '*iso*' product (Eq. (5)).

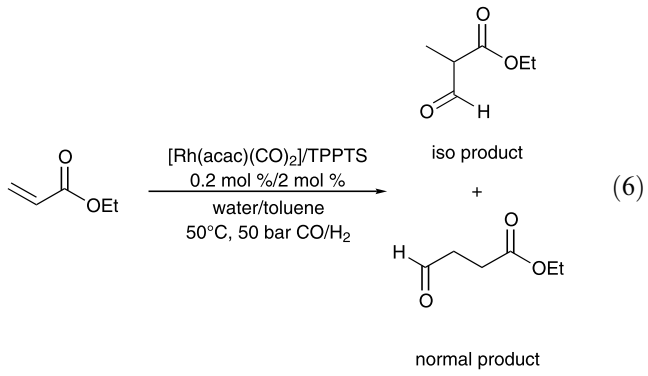


Scheme 1. Hydrogenation of 3-methyl-2-butenal.



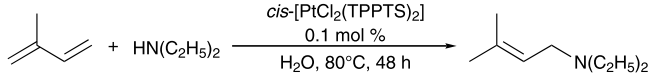
(5)

The hydroformylation of various acrylic esters with a rhodium precursor, [Rh(acac)(CO)$_2$] (acac = acetylacetone), illustrates a case of a catalytic reaction with an activity and a selectivity better in a two-phase system than in a monophasic system [12]. Of particular note is the hydroformylation of ethyl acrylate (Eq. (6)) that occurs in water/toluene in the presence of [Rh]/TPPTS with a catalytic activity of 1020 h^{-1} and a selectivity of 96.6% towards the formation of the *iso* product, whereas with [Rh]/PPh_3 in toluene, the activity falls down to 150 h^{-1} and the selectivity to 93.5%.



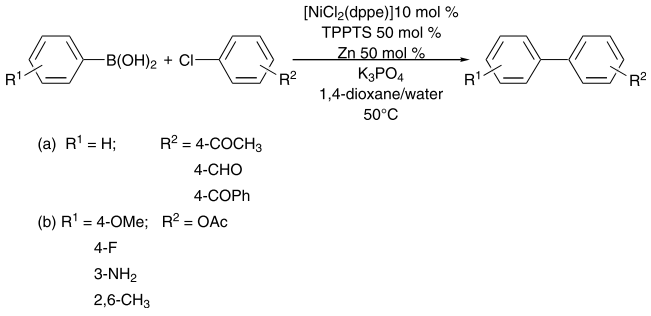
(6)

The water-soluble complex *cis*-[$PtCl_2(TPPTS)_2$]·$6H_2O$ has also been synthesised and used in the 1,4-addition of diethylamine to isoprene in water (Eq. (7)) [13]. At an amine/catalyst ratio of 1000/1, after 48 h, 99% of the amine is consumed with 91% selectivity for the 1,4-product.



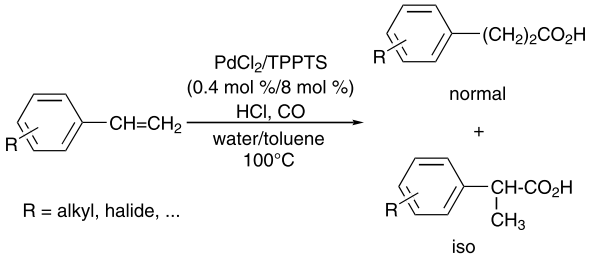
(7)

It is also possible to use a water-soluble nickel(0) catalyst, pre-formed from [$NiCl_2$(dppe)] (dppe = 1,2-bis(diphenylphosphino)ethane) and TPPTS, to perform cross-coupling reactions between arylboronic acids and aromatic chlorides in organo-aqueous media (Eq. (8)) [14]. Phenylboronic acid and aromatic chlorides substituted with electron-withdrawing groups undergo, in the presence of K_2CO_3 in dioxane/water, cross-coupling reactions catalysed by [$NiCl_2$(dppe)]/TPPTS/Zn with good yields (70–80%) (Eq. (8)-(a). It is also possible to couple 4-chloroacetophenone with arylboronic acids bearing electron-donating or electron-withdrawing substituents in moderate-to-excellent yields (47–99%) (Eq. (8)-(b)).



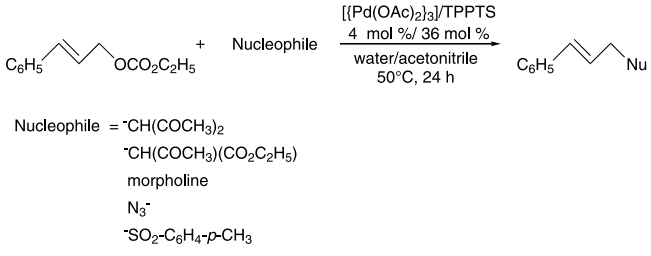
(8)

Amongst the most widely used transition metals in catalytic synthesis of fine chemicals, palladium rapidly took the lead. The palladium dichloride/TPPTS system catalyses the hydroxycarbonylation of various styrene derivatives in the presence of hydrochloric acid and carbon monoxide in aqueous/organic system (Eq. (9)) [15]. For example, the conversions of styrene and 4-acetoxystyrene in water/toluene are total and the normal/*iso* ratios are, respectively, 0.8 and 0.6.



(9)

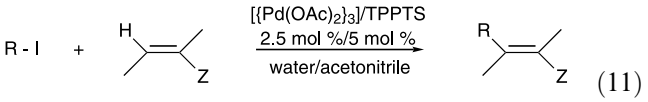
The water-soluble catalyst formed in situ from palladium acetate and TPPTS is an efficient catalyst for substitution of allylic substrates with various carbon nucleophiles and hetero nucleophiles in an aqueous–organic medium [16]. For example, the allylic substitution of substrates shown in Eq. (10) with [{$Pd(OAc)_2$}$_3$] and TPPTS in H_2O/PhCN occurs generally with total conversion.



(10)

It has also been shown that with [{$Pd(OAc)_2$}$_3$] and TPPTS in water/acetonitrile, different carbon–carbon couplings are possible [17]. The coupling of vinyl or aryl iodides with various alkenes (α,β-unsaturated esters or acids, α,β-cyclohexenone, cyclic alkenes)—i.e. the intermolecular Heck reaction—is generally complete within several hours at temperature range of 25–66 °C (Eq.

(11)). Under the same conditions, iodide and bromide precursors derived from cyclohex-2-ene undergo cyclisation, i.e. an intramolecular Heck reaction.

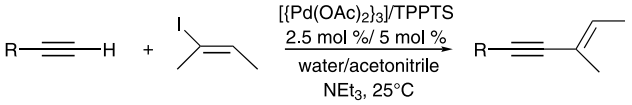


(11)

R = aryl or vinyl

Z = CO_2R^2, CO_2H, COR^3...

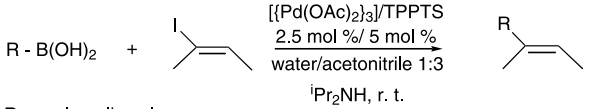
The coupling of a variety of iodoaromatics and vinyl iodides with ethynyltrimethylsilane, propargyl alcohol or ethynylbenzene occurs at 25 °C in the presence of [{Pd(OAc)$_2$}$_3$]/TPPTS and triethylamine with high yields (80–99%) without any CuI promoter (Eq. (12)) [17].



R = $SiMe_3$, CH_2OH, Ph

(12)

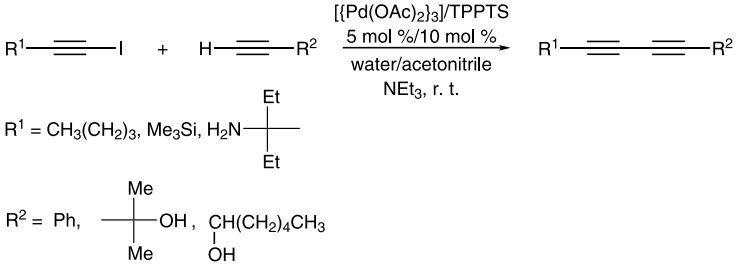
The Suzuki coupling reaction has also been investigated with [{Pd(OAc)$_2$}$_3$]/TPPTS in water/acetonitrile and diisopropylamine as a base (Eq. (13)) [17]. The coupling of alkenyl boronic esters or acids with methyl-3-iodopropenoate, 3-iodocyclopentenone or 3-iodocyclohexenone at room temperature gives good to excellent yields (60–95%).



R = aryl or alkenyl

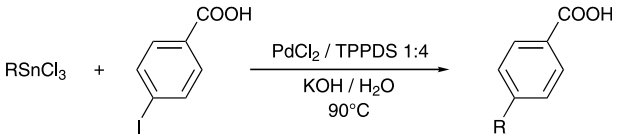
(13)

The system [{Pd(OAc)$_2$}$_3$] and TPPTS in water/acetonitrile also enables the sp-carbon sp-carbon intermolecular coupling reactions at room temperature with triethylamine to afford diynes in yields from 43 to 65% (Eq. (14)) [18].



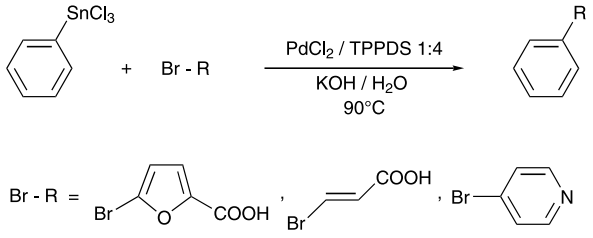
(14)

The disulfonated triphenylphosphine, TPPDS, has been less used than its mono- and trisulfonated counterparts but finds its main application in the aqueous Stille coupling reaction of alkyl-, aryl- and vinyltrichlorostannane derivatives with aryl and vinyl halides [19]. The reaction of 4-iodobenzoic acid with trichlorostannane derivatives, which hydrolyse in aqueous alkaline solution to give $K_n[PhSn(OH)_{3+n}]$ (Eq. (4)), is catalysed by $PdCl_2$/TPPDS and potassium hydroxide in water, and yields the coupling products in about 80% (Eq. (15)). Phenyltrichlorostannane can be coupled under the same conditions to a variety of aryl and vinyl bromides with good to excellent yields (77–96%) (Eq. (16)).



R = Ph, *n*-Bu, CH_3, CH_2=CH, HO_2CCH=CH

(15)



(16)

Many other sulfonated, water-soluble phosphines have been designed for hydroformylation or hydrogenation in two-phase solvent systems with rhodium or ruthenium catalysts and for various reactions with palladium catalysts (Fig. 3).

The hydroformylation of 1-octene in water/methanol can be displayed by the rhodium precursor [Rh(acac)(CO)$_2$] and the water-soluble phosphines 1 ($n = 3$ or 6 [20] and with $n = 10$ [21]) (Fig. 3, Eq. (17)). In the case of the phosphines with $n = 3$ and 6, the hydro-

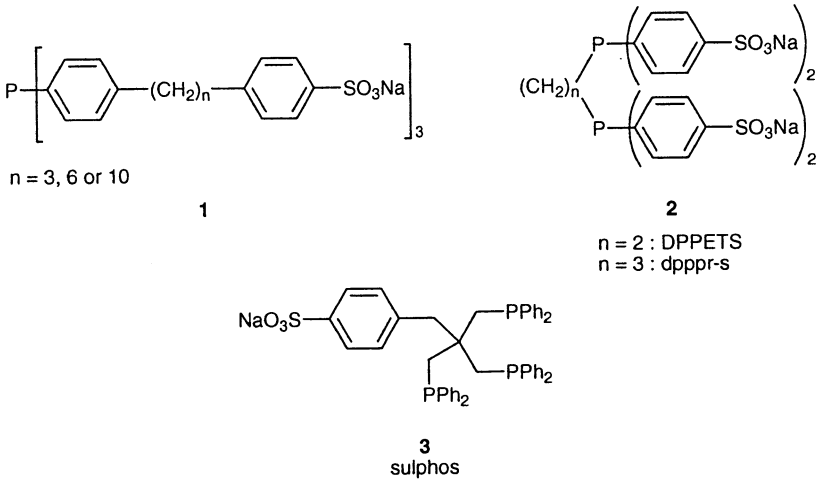
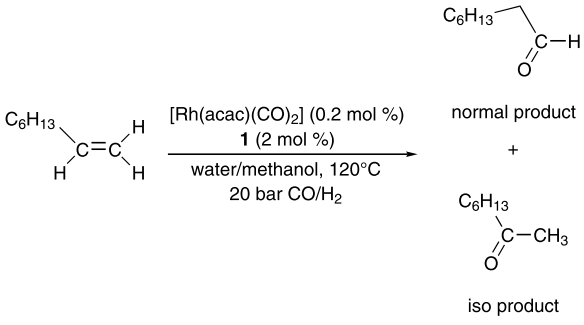


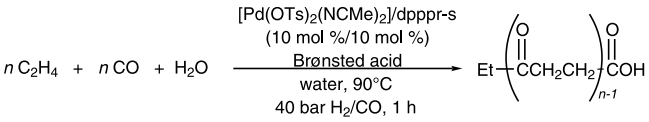
Fig. 3. Sulfonated phosphines.

formylated products (nonanal as the normal product and 2-methyloctanal as the *iso* product) are obtained, respectively, in 85 and 88% yield, with a turnover frequency, TOF, [(mol aldehydes formed) (mol catalyst)$^{-1}$ (h)$^{-1}$] of 71 and 73 h^{-1} and a normal/*iso* ratio of 8.0 and 9.5, respectively. For the phosphine with $n = 10$, the hydroformylation occurs in 80% yield with a TOF of 400 h^{-1} and a normal/*iso* ratio of 82.



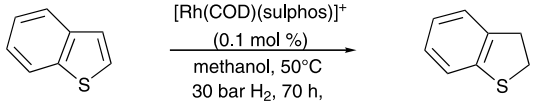
(17)

Conditions similar to the previous ones are used to test the hydroformylation activity of the phosphine 2 with $n = 2$, DPPETS (Fig. 3) [22]. With [Rh(acac)(CO)$_2$] (0.2 mol.%) and DPPETS ([Rh]/DPPETS = 1:3) at 120 °C, $PH_2/CO = 14$ bar in water/methanol, after 15 h the conversion of 1-octene in aldehydes is 22% yield and the normal/*iso* ratio is 3.2. The activity of this phosphine is quite poor, but still in the range of TPPTS. The water-soluble palladium catalyst based on the phosphine 2 with $n = 3$, the 1,3-disulfonated bis(diphenylphosphino)propane, dpppr-s (Fig. 3), catalyses the alternating copolymerisation of carbon monoxide and olefins to poly(ketones) (Eq. (18)) [23]. With dpppr-s/[Pd(OTs)$_2$(NCMe)$_2$] ($OTs^- = p$-CH_3–C_6H_4–SO_3^-) and a Brønsted acid ($CF_3SO_2^-$ or TsO^-, 50 equivalents per palladium) the catalytic activity of the copolymerisation of ethene to carbon monoxide is higher than 4 kg of polymer per g of Pd per h.



(18)

The phosphine sulphos 3 (Fig. 3) forms the complexes [Rh(COD)(sulphos)]$^+$ and [Rh(CO)$_2$(sulphos)]$^+$ with rhodium precursors [24]. The former complex (1 mol.%) catalyses the hydroformylation of 1-hexene in aqueous methanol/*iso*octane at 80 °C, $PH_2/CO = 30$ bar and gives the two aldehydes, heptanal (normal product) and 2-methylhexanal (*iso* product), in a ratio of 69:31. The latter complex, [Rh(CO)$_2$(sulphos)]$^+$, shows catalytic activity towards the hydrogenation of styrene in water/*n*-heptane. With 0.2 mol.% of [Rh] at 65 °C, $PH_2 = 30$ bar, the conversion in ethylbenzene is total after 5 h. Sulphos is also used as a ligand in the complex [Rh(COD)(sulphos)]$^+$, which is a catalyst for the hydrogenation of the benzo[*b*]thiophene in methanol to give 2,3-dihydrobenzo[*b*]thiophene in 50% yield (Eq. (19)) [25].



(19)

A lot of effort has also been directed towards the preparation of chiral, water-soluble diphosphines for the two-phase asymmetric hydrogenation and hydroformylation of prochiral olefins. The chiral products are obtained as the two enantiomers, *R* and *S*, and the enantiomeric excess (ee) is defined as follows:

$$ee = \frac{[M] - [m]}{[M] + [m]}$$

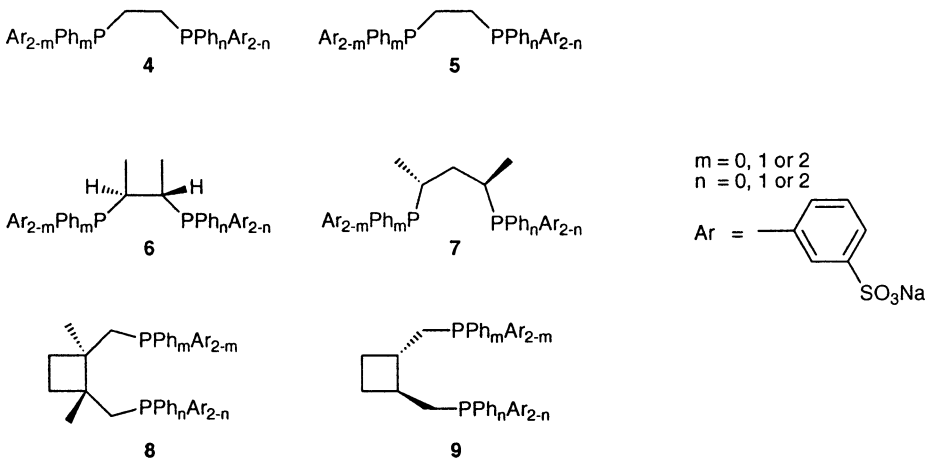


Fig. 4. Chiral sulfonated phosphines.

where [*M*], quantity of the major enantiomer; [*m*], quantity of the major enantiomer.

Rhodium(I) catalysts formed with the sulfonated phosphines 4–9 (Fig. 4) and [{RhCl(COD)}$_2$] (1 mol.% of [Rh], [Rh]/phosphine = 1:1.1) are efficient at room temperature for the asymmetric hydrogenation of carbon–carbon (ee up to 88%), carbon–oxygen (ee up to 28%) or carbon–nitrogen double bonds (ee up to 58%) in aqueous/organic (water/ethyl acetate) two-phase solvent systems [26,27].

The asymmetric hydroformylation of styrene has been performed using [{Rh(μ-OMe)(COD)}$_2$] associated with 7 or 9 (Fig. 4) in water/methanol [28]. The best conditions are with $PH_2/CO = 14$ bar, 0.2 mol.% of [Rh], a [P]/[Rh] ratio of 4 and a temperature range of 50–80 °C. Under these conditions, the phosphines 7 and 9 give, respectively, a conversion of 67 and 48%, a selectivity in aldehydes (2-phenylpropanal as the *iso* product and 3-phenylpropanal as the normal product) of 100 and 98%, an *iso*/normal ratio of 76/24 and 94/6 and an ee of 17 and 2, respectively.

The ligands BISBI have been used commercially in propene hydroformylation since 1990; their sulfonated, water-soluble derivatives BISBIS (Fig. 5) have been prepared and their solubility in water is ca. 1500 g dm^{-3}. In the hydroformylation of propene and 1-hexene in water, these sulfonated diphosphines show, with the rhodium precursor [Rh(OAc)$_3$] (0.03 mol.%), a BISBIS/[Rh] ratio of 7, $PH_2/CO = 50$ bar and at temperatures between 125 and 145 °C, high activity and high selectivity towards the normal aldehyde [29]. For propene, the activity [(mol aldehydes) (g atom Rh)$^{-1}$ (min)$^{-1}$] is 97.7 mol g^{-1} min^{-1}, the selectivity in aldehydes (butanal as the normal product and 2-methylpropanal as the *iso* product) 87% and the normal/*iso* ratio 97/3. For the 1-hexene, the activity is 10.7 mol g^{-1} min^{-1}, the selectivity in aldehydes (heptanal as the normal product and 2-methylhexanal as the *iso* product) 30.3% and the normal/*iso* ratio 95/5.

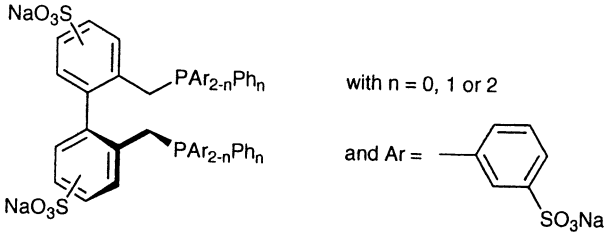
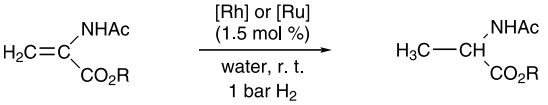


Fig. 5. The phosphines BISBIS.

The sulfonation of the diphosphines NAPHOS leads to the formation of the water-soluble BINAS (Fig. 6) [30–33].

The phosphine BINAS-4 forms with a rhodium precursor the complex [Rh(BINAS-4)(solvent)$_2$]$^+$, which promotes, in water, the asymmetric hydrogenation of prochiral 2-acetamidoacrylic acid and its ester derivative (Eq. (20)) [30]. The reduced products are obtained with total conversion and ee up to 60%. The ruthenium complex [RuCl$_2$(BINAS-4)] shows, under the same conditions, even better catalytic properties towards the asymmetric hydrogenation of prochiral 2-acyl-aminoacids derivatives, the conversions are also total and the ees are up to 85% [31].



(20)

R = H or Me

BINAS-6 shows activities in the aqueous/organic rhodium-catalysed asymmetric hydroformylation of styrene [32]. At 40 °C, $PH_2/CO = 100$ bar, with [Rh(acac)(CO)$_2$] (0.3 mol.%) and [Rh]/BINAS-6 = 1:4 in aqueous methanol/toluene, the conversion of styrene after 25 h is 92%, the selectivity towards the *iso* product 95% and the ee 18%.

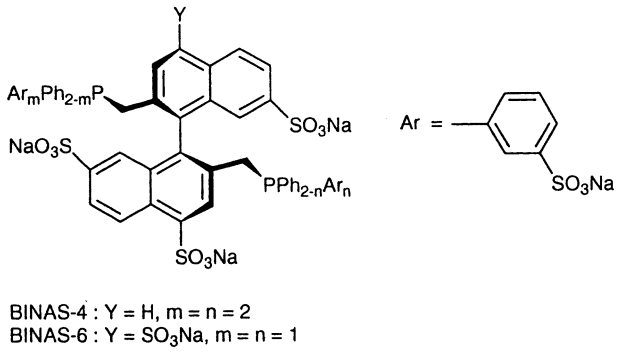
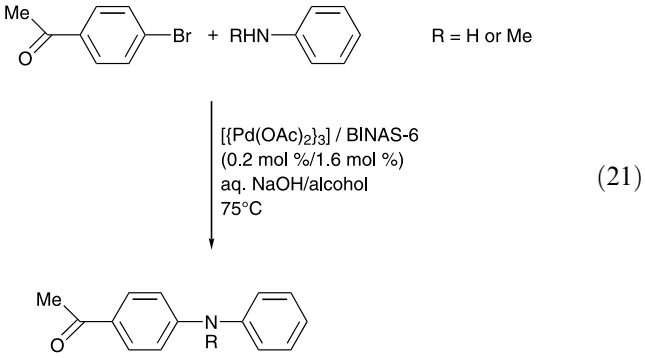


Fig. 6. The phosphines BINAS.

The BINAS-6 ligand is also used for the palladium-catalysed amination of aromatic halides (the Buchwald–Hartwig reaction) in water/methanol (Eq. (21)) [33]. In the presence of $[\{Pd(OAc)_2\}_3]$ and BINAS-6, the coupling reaction of the bromoacetophenone with the amines occurs in yields from 71 to 91%.



(21)

Some more 'exotic' water-soluble sulfonated phosphines have been synthesised; the water-soluble diphosphine **10** based on a xanthene-type backbone (Fig. 7) shows, with a rhodium precursor, catalytic activity towards the hydroformylation of propene or 1-hexene in water where it retains the exceptional selectivity towards the linear aldehyde (butanal and heptanal) observed with xantphos (the xanthene phosphine) in non-aqueous solvents [34]. With 0.01 mol.% of $[Rh(H)(CO)(PPh_3)_3]$, [Rh]/[**10**] = 5:1, at 120 °C and $PH_2/CO = 10$ bar, propene is converted in 67% yield, the selectivity towards aldehydes (butanal as the normal product and 2-methylpropanal as the *iso* product) is total, the normal/*iso* ratio is 30.2 and the TOF 140 h^{-1}. The conditions for the hydroformylation of 1-hexene are similar, $[Rh(H)(CO)(PPh_3)_3]$ (0.03 mol.%), [Rh]/[**10**] = 5:1, at 120 °C and $PH_2/CO = 19$ bar. Under these conditions, 1-hexene is transformed in 13% yield, the selectivity towards aldehydes (heptanal as the normal product and 2-methylhexanal as the *iso* product) is also total, the normal/*iso* ratio is 34.7 and the TOF 9 h^{-1}.

The sulfonated dibenzofuran phosphines **11** (Fig. 7) have been synthesised by Sollewijn et al. and their solubilities in water are 80 g dm^{-3} with $n = 1$, 800 g dm^{-3} with $n = 2$ and over 1 kg dm^{-3} with $n = 3$. In combination with 5 mol.% of palladium acetate ([P]/[Pd] = 3:1) and triethylamine or sodium acetate as a base, they catalyse carbon–carbon coupling reactions in water/acetonitrile [35]. Over a temperature range of 40–95 °C, the Heck coupling of aryl iodides with alkenes (cf. equation 11) occurs in yields from 50 to 97% and the Suzuki reaction of phenyl boronic acid with aryl iodides (cf. equation 13) yields the coupling products in 58–90%. The phosphines **11** also show catalytic activities towards the rhodium catalysed two-phase hydroformylation of propene in water [35]. With $[Rh(acac)(CO)_2]$ (0.01 mol.%), [Rh]/[**11**] = 1:10 at 120 °C and $PH_2/CO = 10$ bar, the three phosphines **11** show 100% of selectivity to aldehydes and the phosphine with $x = 1$ gives the best results with a TOF of 93 h^{-1} and a normal/*iso* ratio of 3.7.

1.2. Phosphines functionalised with ammonium groups

Amphiphilic phosphines can also be obtained from the quaternisation of the nitrogen atom of aminoalkyl or aminoaryl phosphines. The main example of this class of phosphine is 'AMPHOS' (Fig. 8). The treatment of $[\{RhCl(NBD)\}_2]$ (NBD = norbornadiene) with AMPHOS nitrate gives the complex $[Rh(NBD)(AMPHOS)_2]^{3+}$. This complex shows catalytic activity in water/ethyl acetate for the hydrogenation of 1-hexene and styrene as well as for the hydroformylation of 1-hexene [36]. With $[\{RhCl(NBD)\}_2]$ (0.1 mol.%), [Rh]/[amphos] = 1:2, $PH_2 = 3$ bar, at 25 °C for 6 h, the catalytic activity of the complex for the reduction of styrene to ethylbenzene is 71 and 84 h^{-1} for the

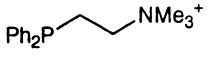
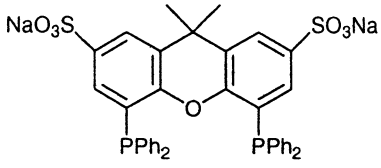


Fig. 8. The phosphine AMPHOS.



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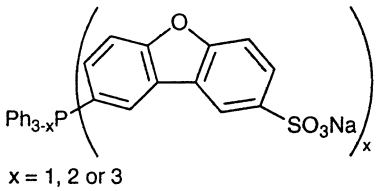


11

Fig. 7. Sulfonated diphosphines.

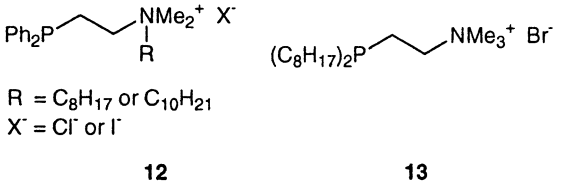


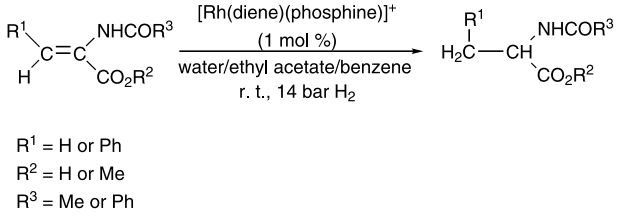
Fig. 9. Phosphines with quaternised ammonium groups.

hydrogenation of 1-hexene to hexane. With 0.4 mol.% of [{RhCl(NBD)}$_2$], a [Rh]/[amphos] ratio of 1:3, PH_2/CO = 40 bar, at 90 °C for 24 h, the complex catalyses the hydroformylation of 1-hexene with a total conversion, a selectivity in aldehydes of 96% and a normal/*iso* ratio of 1.7.

Other monocationic amphiphilic tertiary phosphines, **12** and **13** (Fig. 9), have been synthesised and with palladium dibromide they form water-soluble palladium complexes [37].

The idea of inducing hydrophilicity in phosphines by adding a quaternised ammonium group has then been extended to chiral ligands, such as **14**–**16** (Fig. 10) [38].

Rhodium complexes of these ligands show catalytic activities towards the asymmetric hydrogenation of dehydroamino acid derivatives in water/ethyl acetate/benzene systems (Eq. (22)) [39]. With [Rh(diene)(phosphine)][BF_4] (diene = COD or NBD), the conversion in the reduced products is total with the three phosphines. With (*R,R*)-DIOP as a ligand, the ees are rather low (8–67%), with (*S,S*)-BDPP the ees are a bit higher (40–79%). However, the best results are obtained with (*S,S*)-chiraphos, which gives ees from 58 to 98%.



(22)

Another way of inducing water-solubility in phosphines is to add amino groups, for example to the bis[2-(diphenylphosphino)ethyl]ether, POP, to form POPam **17** (Fig. 11) or to xantphos to form the xantham **18** (Fig. 11) [40]. With the rhodium precursor [Rh(acac)(CO)$_2$] (0.02 mol.%), a [Rh]/[P] ratio of 1:10 at 80 °C and 20 bar of H_2/CO pressure in toluene, the hydroformylation of 1-octene shows with **17** and **18**, respectively, a conversion of 71 and 68%, a selectivity to aldehydes of 100 and 96%, a normal/*iso* ratio of 7 and 49 and a TOF of 171 and 136 h^{-1} is observed. Under the same conditions, the phosphine 18 can also take part in the hydroformylation of 1-hexene, with a conversion of 71%, a selectivity to aldehydes of 96.8%, a normal/*iso* ratio of 48 and a TOF of 142 h^{-1}.

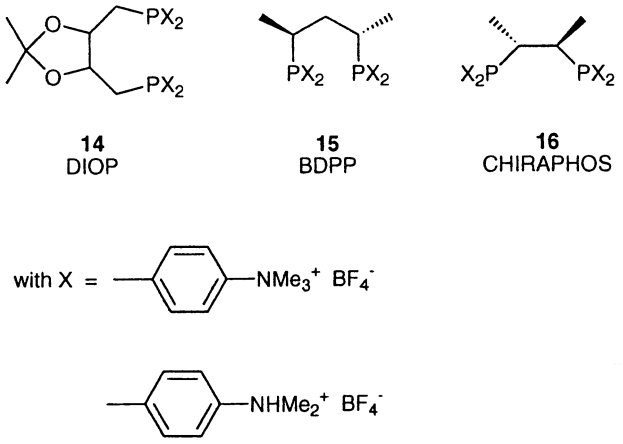
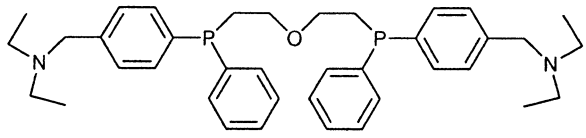


Fig. 10. Chiral phosphines with quaternised ammonium groups.

The phosphine N3P **19** (Fig. 12) also presents water-solubility properties and displays, in water/toluene, catalytic properties for the hydroformylation of 1-hexene with the rhodium precursor [Rh(acac)(CO)$_2$] (0.1 mol.%), [Rh]/[**19**] = 1:10, at 80 °C and PH_2/CO = 20 bar. After 16 h the conversion is 32%, the TOF 20 h^{-1} and the normal/*iso* ratio 2.8 [41]. These results are not as good as those obtained in a monophasic system; in toluene, after 1 h, the conversion of 1-hexene is 57%, the TOF 736 h^{-1} and the normal/*iso* ratio 2.8. However, as it is possible to separate the catalyst from the product by a simple decantation when the reaction is run in water/toluene, doing the reaction in a biphasic system is still a valuable application.



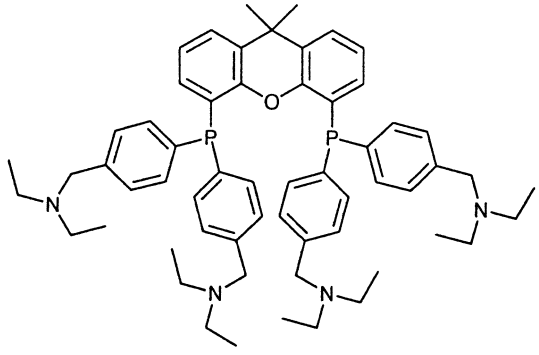


Fig. 11. Phosphines with amino groups.

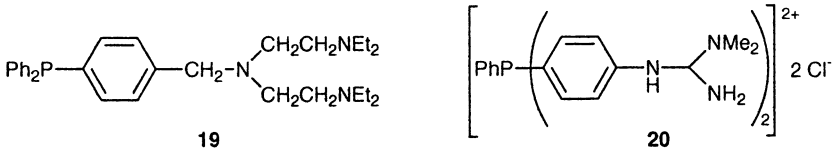
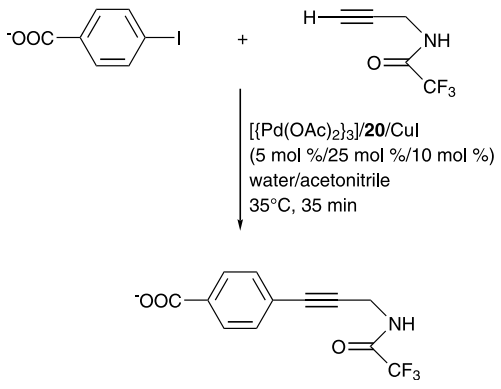


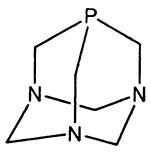
Fig. 12. Triphenylphophines substituted by ammonium groups.

The cationic phosphine **20** (Fig. 12) bearing guanidinium functions has also been reported [42]; the introduction of one of more hydrophilic groups to triphenylphosphine adds pronounced hydrophilicity to the ligand. The phosphine **20** exhibits, in the presence of a palladium precursor, catalytic activity towards the Suzuki coupling reaction (cf. Eq. (13)) [42b]. The substrate, *m*-bromophenyldiphenylphosphine oxide, reacts with *p*-tolylboronic acid in the presence of $[Pd(PPh_3)_4]$/**20** (1/20 mol.%) in aqueous ethylene glycol/toluene with potassium carbonate as the base, to yield the 4-methyl-1,1′-biphenyl-substituted phosphine oxide in 100% yield after 60 h; that is slower than with TPPMS, which gives a total conversion after only 10 h. However, the guanidiniumphenylphosphine **20** shows better catalytic activities than TPPMS in the palladium-catalysed Castro–Stephens–Sonogashira reaction (Eq. (23)) [42]. The coupling of *p*-iodobenzoic acid and *N*-(trifluoroacetyl)propargylamine in water/acetonitrile is catalysed by $[\{Pd(OAc)_2\}_3]$/**20**/CuI with triethylamine as a base and occurs with a total conversion after 35 min, whereas with TPPMS the conversion is less than 10% after 2 h.



(23)

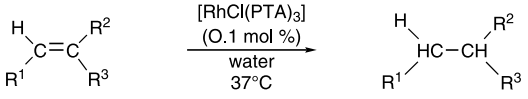
Recently, it has been found that 1,3,5-triaza-7-phosphaadamantane (PTA) (Fig. 13) is, in terms of water-solubility, analogous to TPPMS.



PTA

Fig. 13. 1, 3, 5-Triaza-7-phosphaadamantane.

The complex of ruthenium(II), *cis*-$[RuCl_2(PTA)_4]$ has been prepared from ruthenium trichloride and PTA [43] and the complex [RhCl(PTAH)(PTA)]Cl has been synthesised from rhodium dichloride and PTA [44]. Those two complexes are effective catalysts for the regioselective hydrogenation of unsaturated aldehydes in water/chlorobenzene with sodium formate as a source of hydrogen. The complex *cis*-$[RuCl_2(PTA)_4]$ (0.1 mol.%) displays, at 80 °C, the regioselective conversion of unsaturated aldehydes to unsaturated alcohols, up to 87.6% yield for the reduction of 2-butenal in 2-butenol [43]. One mole percent of [RhCl(PTAH)(PTA)]Cl catalyses the regioselective hydrogenation of unsaturated aldehydes to the corresponding saturated adehydes at 70 °C, with a conversion up to 93.9% for the reduction of *trans*-cinnamaldehyde to 3-phenylpropanal [44]. Another water-soluble complex formed with the phosphine PTA is $[RhCl(PTA)_3]$, which is an active catalyst for hydrogenation of various olefinic acids and allyl alcohol in water (Eq. (24)) [45]. With $[RhCl(PTA)_3]$ (1 mol.%) at 37 °C, the TOF of the reaction is rather low for maleic acid (about 50 h^{-1}) but very good for fumaric and crotonic acids (about 335 h^{-1}).



Crotonic acid:	$R^1 = CH_3$,	$R^2 = H$,	$R^3 = CO_2H$
Maleic acid:	$R^1 = CO_2H$,	$R^2 = H$,	$R^3 = CO_2H$
Fumaric acid:	$R^1 = CO_2H$,	$R^2 = CO_2H$,	$R^3 = H$
Itaconic acid:	$R^1 = H$,	$R^2 = CO_2H$,	$R^3 = CH_2CO_2H$
Allyl alcohol:	$R^1 = H$,	$R^2 = H$,	$R^3 = CH_2OH$

(24)

1.3. Phosphines containing carboxylate groups

Phosphines with carboxylate groups are some of the earliest investigated water-soluble phosphines, indeed the phosphine **21** (Fig. 14) was synthesised by Mann et al. as early as 1952 [46]. The carboxylated phosphine **22** (Fig. 14), synthesised by Jegorov et al., possesses the property of being extractable from benzene into water [47].

The carboxylated phosphines analogous of the triphenylphosphines, the phosphines **23** (Fig. 14), have been complexed to platinum [48] and to rhodium [49].

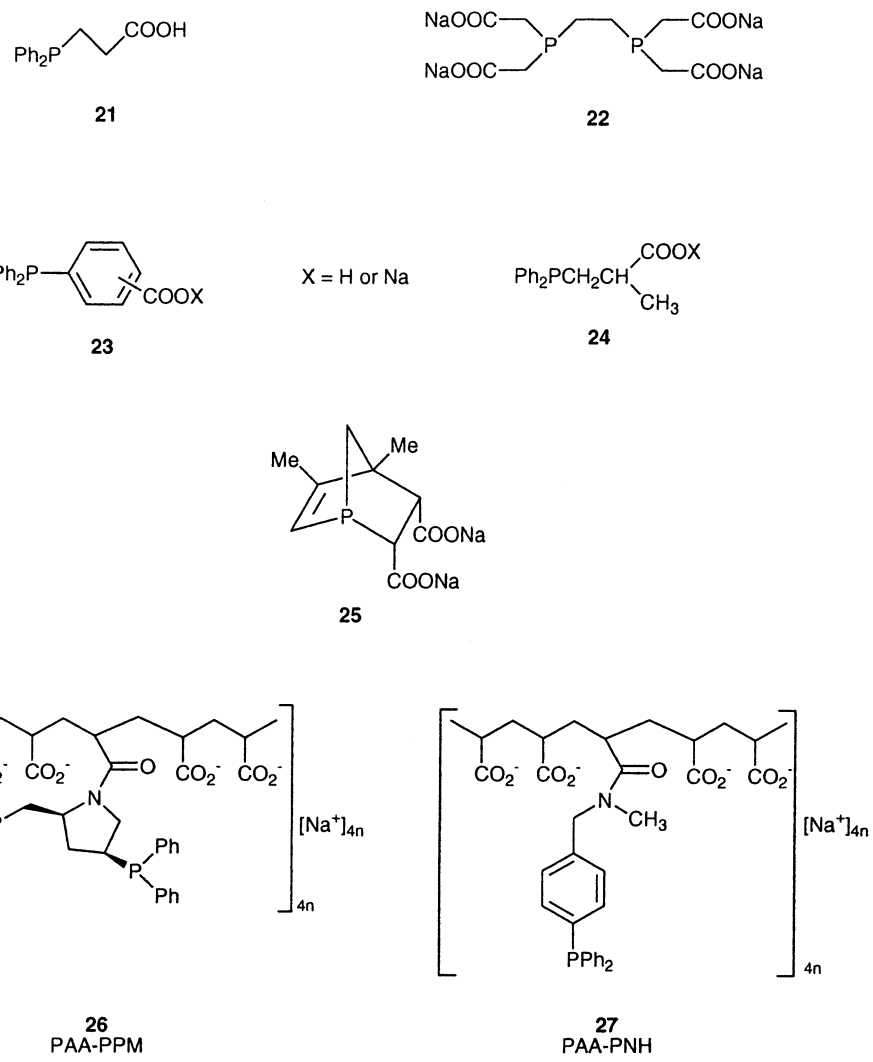
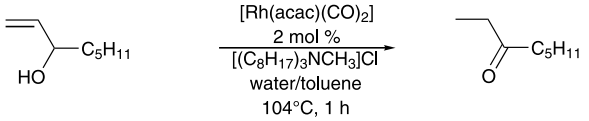


Fig. 14. Phosphines with carboxylate groups.

The sodium salts of [RhCl(COD)(**23**)], (2 mol.%), catalyse the isomerisation of 1-octen-3-ol to 3-octanone in water/toluene with $[(C_8H_{17})_3NCH_3]Cl$ as a transfer agent (Eq. (25)). After 1 h, the conversion of 1-octen-3-ol is from 35 to 54%, except with the phosphine $Ph_2P(C_6H_4$-2-COOH), which gives a very good conversion of 96% [49].

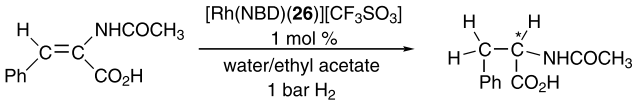


(25)

With the rhodium precursor $[Rh(acac)(CO)_2]$, the phosphines **24** (Fig. 14) possess catalytic activities in the hydrogenation and hydroformylation of 1-hexene [50]. In the presence of the phosphine **24** (X = H) in water/ethanol, at 80 °C, $PH_2 = 10$ bar, [Rh]/[**24**] = 0.1/1.1 mol.%, 99% of 1-hexene is hydrogenated in hexane. Under similar conditions, in water/toluene, at 80 °C, $PH_2/CO = 10$ bar, [Rh]/[**24**] (X = H)] = 0.1/1.1 mol.%, the hydroformylation of 1-hexene occurs in only 2% conversion. However, with the sodium salt of the phosphine **24** (X = Na), the conversion of 1-hexene is increased to 92%, with a selectivity towards the aldehydes of 94% and a normal/*iso* ratio of 2.4.

The phospha-norbornene **25** (Fig. 14), synthesised by Mercier et al., is very water-soluble (≥ 300 g dm^{-3}) [51] as well as the polymers PAA–PPM **26** and PAA–PNH **27** (Fig. 14), synthesised by Malmstöm et al., which possess a solubility in water of about 115 g dm^{-3} [52]. PAA–PPM **26** forms, with a rhodium precursor, the complex [Rh(NBD)(**26**)][CF_3SO_3], which hydrogenated, at 1 mol.% in water/ethyl acetate, (*Z*)-2-acetamido

cinnamic acid in 97%, with an ee of 74% (Eq. (26)) [53].

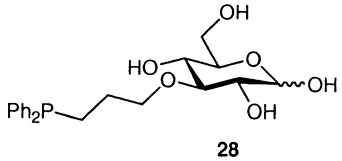


(26)

With $[Rh(acac)(CO)_2]$, PAA–PNH **27** exhibits catalytic activity towards the hydroformylation of 1-hexene and 1-octene in water/toluene [54]. At 60 °C, PH_2/CO = 40 bar, in water/toluene with SDS (sodium dodecylsulphate) as a phase-transfer agent, a mixture of $[Rh(acac)(CO)_2]$ and **27** (0.4/1.6 mol.%) gives, after 20 h, a total conversion in the aldehydes derived from 1-hexene, with a normal/*iso* ratio of 2.2. For the hydroformylation of 1-octene, larger quantities of catalyst are required, $[Rh(acac)(CO)_2]$/**27** = 1/3 mol.%, but after only 6 h it gives 100% of the aldehydes with a normal/*iso* ratio of 3.

1.4. The case of phosphines with carbohydrate groups

The carbohydrates constitute an interesting type of hydrophilic groups and a few examples have been described in the literature. In the compound **28** (Fig. 15), the hydroxy group of the carbohydrate is attached to a diphenylphosphinopropyl moiety to induce water-solubility (about 80 g dm^{-3}) [55]. The phosphines **29**, **30** and **31** (Fig. 15) contain β-cyclodextrin as a sugar component [56,57]. The bidentate ligand with a 2-(diphenylphosphinoethyl)-thiol moiety attached to a β-cyclodextrin, **29**, gives the corresponding norbornadiene rhodium(I) complex in the form of the BF_4^- salt from the precursor $[\{RhCl(NBD)\}_2]$ [56]. The β-cyclodextrin-modified diphosphines **30** and **31** display, with $[Rh(COD)_2][BF_4]$ in 30% aqueous DMF, the hydroformylation of 1-octene [57]. With [Rh]/[P] (0.03/0.03 mol.%), at 60 °C and PH_2/CO = 100 bar, after 18 h the



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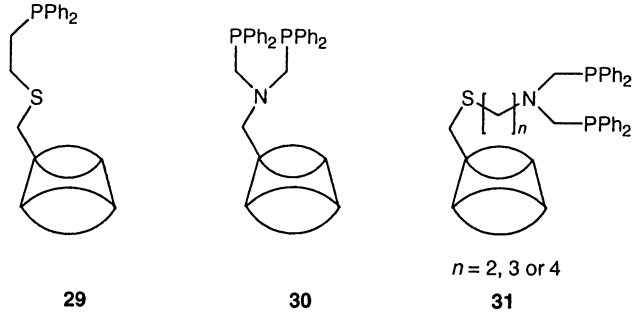
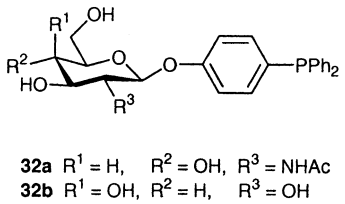


29 **30** **31**

Fig. 15. Phosphines with carbohydrate groups.



32a R^1 = H, R^2 = OH, R^3 = NHAc
32b R^1 = OH, R^2 = H, R^3 = OH

Fig. 16. The 1-*O*-glycosides of hydroxytriarylphosphines.

conversion of the alkene and the selectivity in aldehydes are higher than 99%, the TOF are about 182 h^{-1} and the selectivities in favour of the normal product are up to 76%.

Another class of carbohydrate-containing water-soluble ligands are the 1-*O*-glycosides of hydroxytriarylphosphines **32a** and **32b** (Fig. 16). They catalyse, with palladium acetate (0.01 mol.%) and [Pd]/[P] = 1:3, at 78 °C for 2 h in the presence of sodium carbonate, the Suzuki coupling reaction of phenyl boronic acid with 4-bromoacetophenone and 1-bromo-4-chlorobenzene in aqueous methanol/toluene (cf. Eq. (13)) [58,59]. With bromoacetophenone, the yields are ca. 90% and the TOF 4500 h^{-1} for the two phosphines **32**. With 1-bromo-4-chlorobenzene, the phosphines **32a** and **32b** give, respectively, yields of 56 and 71% and TOF of 2800 and 3550 h^{-1}. The same catalyst $([\{Pd(OAc)_2\}_3]$/**32** (0.01/0.03 mol.%) is also efficient for the Heck coupling reaction of styrene with 4-bromoacetophenone and 1-bromo-4-nitrobenzene in the presence of sodium acetate in xylene/ethylene glycol (cf. equation 11) [58,59]. At 130 °C, after 20 h, the phosphines **32a** and **32b** give, respectively, the bromoacetophenone in 98 and 80% yield and TOF of 4.9 and 4 h^{-1}. With 1-bromo-4-nitrobenzene, **32a** and **32b** give similar yields of 85% and TOF of 42.5 h^{-1}. The phosphine **32a**, with $[Rh(OAc)_3]$, also displays catalytic properties towards the hydroformylation of 1-octene in water/toluene [59]. After 2 h at 125 °C, PH_2/CO = 25 bar, with $[Rh(OAc)_3]$/**32a** = 0.1/1 mol.%, 95% of 1-octene is converted into aldehydes with a total selectivity, a normal/*iso* ratio of 2.4 and a TOF of 475 h^{-1}.

1.5. Phosphonium and phosphonate groups

A new class of water-soluble phosphines, named 'Phosphos' (Fig. 17), was found in 1991 by Baird et al. [60]. With the rhodium precursor $[\{RhCl(NBD)\}_2]$, they give rhodium complexes of the type $[Rh(NBD)(Phosphos)_2][NO_3]_3$. Those complexes (0.1 mol.%) exhibit good activity in the hydrogenation of 1-hexene in water at 3 bar of hydrogen pressure. With the phosphos (n = 2, 3 and 10) after 6 h, the conversions are, respectively, 45,

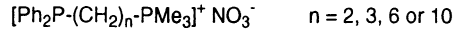


Fig. 17. The phosphines phosphos.

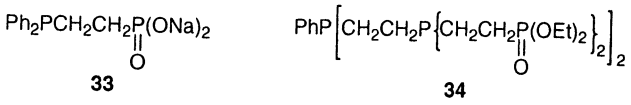
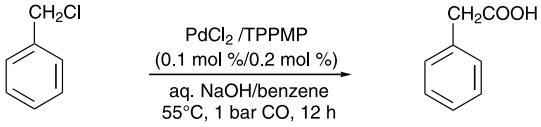


Fig. 18. Phosphines with phosphonate groups.

100 and 70% and the selectivities in hexane 51, 70 and 39%. However, the phosphine with $n = 6$ gives the best results, in only 3 h, with a conversion of 99% and a selectivity of 90%.

It is also possible to induce hydrophilicity in phosphines by substituting them with phosphonate groups. For example, the phosphines **33** or **34** (Fig. 18) have a high solubility in water, as do their palladium complexes [$PdBr_2$(**33**)] and [Pd(**34**)(CH_3CN)][BF_4]$_2$ [61,62].

The triphenylphosphine monophosphonate TPPMP (Fig. 19), synthesised by Schull et al., possesses a solubility in water of 0.38 g dm^{-3} [63]. In the presence of palladium dichloride and sodium hydroxide in water/benzene, with tetrabutylammonium iodide as a phase-transfer agent, it displays catalytic activity towards the carbonylation of benzyl chloride, to give phenylacetic acid in 91% yield (Eq. (27)).



(27)

1-Phosphanorbornadiene has been substituted in the β-position with a phosphoric acid function to exhibit a water-solubility of 230 g dm^{-3}. The corresponding sodium salt, **35** (Fig. 20), is a good ligand for the hydroformylation of 1-hexene in water/toluene. With [{$RhCl(CO)_2$}$_2$]/**35** (1/2 mol.%) at 80 °C with PH_2/CO = 20 bar, the aldehydes are obtained in 89% with a normal/*iso* ratio of 0.88 [64].

1.6. Phosphines with hydroxyalkyl or polyether groups

It has been shown that hydroxyalkyl-substituted phosphines are soluble in water only if they carry several hydroxyalkyl groups. The commercially available water-soluble tris(hydroxymethyl)phosphine $P(CH_2OH)_3$ was

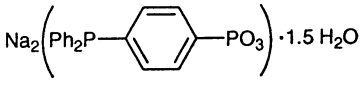


Fig. 19. The phosphine TPPMP.

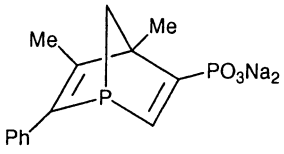
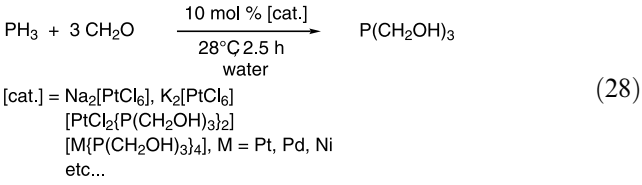


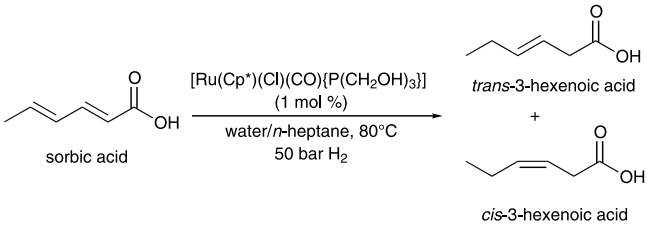
Fig. 20. The 1-phosphanorbornadiene substituted by phosphoric acid.

first complexed to transition metals (platinum, palladium or rhodium) in 1973 by Chatt et al. and exhibits, with the rhodium precursor [{RhCl(cyclohexene)$_2$}$_2$], catalytic activity in the hydrogenation in ethanol of 1-octene in octane with total conversion [65]. It has also been shown that tris(hydroxymethyl)phosphine forms water-soluble complexes with platinum, palladium or nickel, which are catalysts for the production of the ligand itself from addition of phosphine (PH_3) to aqueous formaldehyde (Eq. (28)) [66].



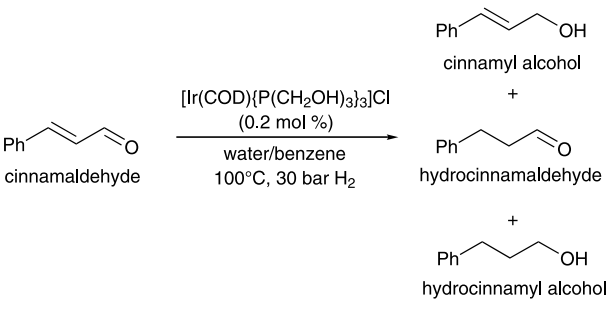
(28)

Some ruthenium complexes with tris(hydroxymethyl)phosphine as a ligand have been synthesised and exhibit catalytic activities in the hydrogenation of sorbic acid (Eq. (29)) [67]. In the presence of [Ru(Cp*)(Cl)(CO){$P(CH_2OH)_3$}] (Cp*H = 1,2,3,4,5-pentamethylcyclopentadiene), sorbic acid is reduced with a TOF of 2.6 h^{-1}, leading in 15 h to the formation of 3-hexenoic acid in 40% with a *cis*/*trans* ratio of 4. These results are not exceptional but are still better than with TPPTS.



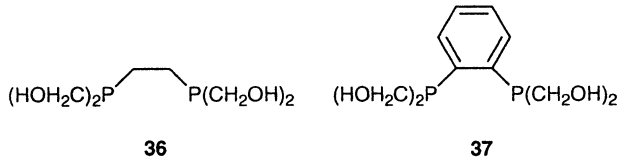
(29)

Fukuoka et al. synthesised the iridium complex of the phosphine $P(CH_2OH)_3$, [Ir(COD){$P(CH_2OH)_3$}$_3$]Cl, that exhibits catalytic activities towards the hydrogenation of cinnamaldehyde in water/benzene to give the reduced compounds in 90%, with 76% of cinnamyl alcohol, 2% of hydrocinnamaldehyde and 22% of hydrocinnamyl alcohol (Eq. (30)).



(30)

The rhodium complex of $P(CH_2OH)_3$, *cis*-



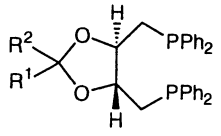
36 37

Fig. 21. Diphosphines with hydroxymethyl groups.

$[RhH_2\{P(CH_2OH)_3\}_4]Cl$ (1 mol.%), shows catalytic properties for the hydroformylation of 1-pentene in water/toluene [68]. At 100 °C, $PH_2/CO = 40$ bar, after quantitative conversion (20 h), the composition of the mixture was 43% of hexanal (normal product) and 57% of 2-methylpentanal (*iso* product).

The idea of using hydroxymethyl groups to induce hydrophilicity in phosphines has been extended to many diphosphines, such as **36** and **37** (Fig. 21), which are also water-soluble [69]. Some additional examples have been reviewed by Katti et al. [70].

The chiral phosphines analogous to DIOP substituted by hydroxyl groups, **38** (Fig. 22), have been synthesised and their rhodium complexes, $[Rh(COD)(\mathbf{38})][BF_4]$ (2 mol.%), display asymmetric hydrogenation of methyl-(*Z*)-2-*N*-acetamidocinnamate, at 25 °C and $PH_2 = 1$ bar, in methanol, to give the reduced product in 100% of conversion and an ee about 70% [71].



$R^1 = CH_2OH$

$R^2 = CH_3$ or C_6H_5

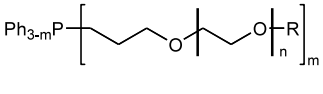
38

Fig. 22. The hydroxyl-substituted DIOP.

Some water-soluble hydroxyalkyl- or poly(ether)-substituted phosphines have also been synthesised, such as the ethyl glycol derivatives **39** (Fig. 23) [54]. The phosphines **40** (Fig. 23) are also water-soluble as are their complexes with nickel, rhodium and ruthenium [72]. Okano et al. have synthesised the poly(ether)-substituted amphiphilic phosphines 41 (Fig. 23) [73]. The phosphines **41** with R = H have solubilities in water at 30 °C of 65 g dm^{-3} with $n = 1$, of 110 g dm^{-3} with $n = 2$ and over 200 g dm^{-3} with $n = 3$. With R = Me, the water-solubilities are 1.9 g dm^{-3} with $n = 1$, of 11 g dm^{-3} with $n = 2$ and over 200 g dm^{-3} with $n = 3$. The water-soluble phosphines **42** and **43** (Fig. 23) have been synthesised by Valls et al., as have their ruthenium complexes [74].

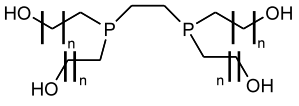
Diphosphines substituted by poly(ether) chains **44** (Fig. 24) complexed to a transition metal lead to the formation of water-soluble metallacrown ethers, such as *cis*-$[M(CO)_4\{Ph_2P(OCH_2CH_2)_nOPPh_2\}]$ with M = Cr, Mo or W and $n = 2$–5, [75] M = Mo or Pt and $n = 3$–5, [76,77] M = Pd and $n = 4$ [78].

As seen previously, a large number of hydrophilic hydroxyalkyl- or poly(ether)- substituted phosphines has been reported in the literature; however, very few of them have been tested in catalysis. Crown-ether substituted ligands, such as **45** (Fig. 25) are one of the rare examples; combined with $[PdCl_2(PhCN)_2]$, they form the complexes *trans*-$[PdCl_2(\mathbf{45})_2]$, that, with $n = 3$, exhibit catalytic activity in the hydrogenolysis of 1-(chloromethyl)naphtalene to 1-methylnaphthalene in a benzene/aqueous formate with 63% yield (Eq. (31)) [73]. With [Pd] = 0.5 mol.% at 60 °C, with $n = 3$, the yield is 63%.



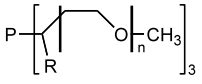
m = 1 or 2
n = 1, 2 or 3

39



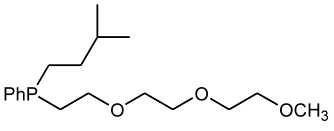
n = 0, 2, 3 or 4

40

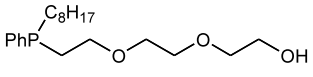


R = H or Me
n = 1, 2 or 3

41

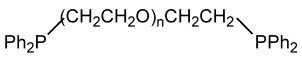


42



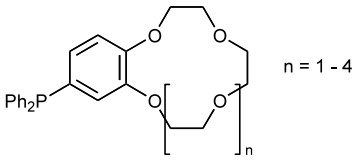
43

Fig. 23. Polyether-substituted phosphines.



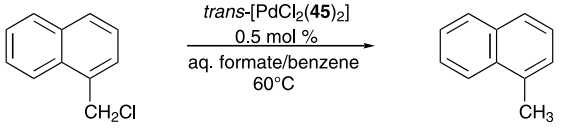
44

Fig. 24. Diphosphines substituted by polyether chains.



45

Fig. 25. Crown-ether substituted phosphines.



(31)

1.7. Comparison of the phosphines

Several examples given previously show water-soluble phosphines which induce hydrophilicity in the transition-metal complexes bearing them. This hydrophilicity enables the reactions catalysed by these complexes to be conducted in aqueous/organic two-phase systems. In order to compare the efficiency of the various phosphines as ligands in some of the main catalytic reactions, the hydroformylation of 1-octene and 1-hexene or the hydrogenation of styrene and 1-hexene, the reactions conditions as well as the results of the reactions are collected together in Tables 1–4. As seen previously, (Eq. (5)), the hydroformylation of terminal alkenes leads to the formation of a normal product, the *n*-aldehyde, and an *iso* product, the *i*-aldehyde. Thus, the rhodium-catalysed hydroformylation of 1-octene in an aqueous/organic two-phase system leads to the formation of the *n*-aldehyde, nonanal, and the *i*-aldehyde, 2-methyloctanal, while the hydroformylation of 1-hexene leads to the formation of heptanal as the *n*-product and 2-methylhexanal as the *i*-product. Several phosphines have been tested in these two catalytic reactions with different rhodium precursors, under different conditions. Table 1, for the hydroformylation of 1-octene, and Table 2, for the hydroformylation of 1-hexene, summarise the reaction conditions for each phosphine: the catalyst precursor used [catalyst precursor], the quantity of catalyst used (in mol per 100 mol of substrate) [catalyst (mol.%)], the phosphine/catalyst ratio [phosphine/catalyst], the pressure of hydrogen/carbon monoxide (in bar) [PH_2/CO (bar)], the temperature of the reaction (in °C) [*T* (°C)], the reaction time (in hours) [*t* (h)], the number of moles of products formed for 100 mol of initial substrate [conversion (%)], the number of moles of normal and *iso* aldehydes formed for 100 mol of products formed [selectivity (%)], the normal/*iso* ratio [*n*/*i*], the turnover frequency,(mol aldehydes formed) (mol catalyst)$^{-1}$.(h)$^{-1}$ [TOF (h^{-1})] and finally the reference for each phosphine.

Table 1 shows that the phosphine that gives the best result, i.e. the highest TOF, is the phosphine **32a** (Entry 13) with a TOF of 475 h^{-1}. The phosphine 1 with $n = 10$ (Entry 4) also shows a high TOF of 400 h^{-1}. The TOF takes into account the conversion and selectivity in aldehydes as well as the quantity of catalyst used and the reaction time but it ignores the other reaction conditions (the phosphine/catalyst ratio, the pressure of gas or the temperature) and it does not show the normal/*iso* ratio which is important in the results of the hydroformylation reactions. Thus, it is important to note that with the phosphines **30** and **31** (Entry 12), the phosphine/catalyst ratio is only 1:1. However, it is compensated by a higher hydrogen/carbon monoxide pressure of 100 bar to give a moderated TOF of 182 h^{-1}. Another interesting result is shown in Entry 10 with the phosphine **18**, which gives a moderate TOF of 136 h^{-1} but a very high *n*/*i* ratio of 49.

In Table 2 are shown the results for the rhodium-catalysed hydroformylation of 1-hexene with various phosphines. The phosphine that gives the higher TOF is the phosphine **24** (Entry 6) with a TOF of 216 h^{-1}, however, the *n*/*i* ratio is much lower than the phosphine **18** (Entry 4), which shows a very high *n*/*i* ratio of 48 and a TOF, still higher than the other phophines, of 142 h^{-1}.

The hydrogenation of alkenes is also a very classical catalytic reaction. In Tables 3 and 4 are collected, respectively, the conditions and the results of the rhodium-catalysed hydrogenations of styrene and 1-hexene with various phosphines in aqueous/organic two-phase systems. These two tables show, as for the hydroformylation tables, the catalyst precursor used [catalyst precursor], the quantity of catalyst used (in mol per 100 mol of substrate) [catalyst (mol.%)], the phosphine/catalyst ratio [phosphine/catalyst], the pressure of hydrogen (in bar) [PH_2 (bar)], the temperature of the reaction (in Celsius degrees) [*T* (°C)], the reaction time (in h) [*t* (h)], the number of moles of products formed for 100 mol of initial substrate [conversion (%)], the turnover frequency, which is (mol aldehydes formed) (mol catalyst)$^{-1}$ (h)$^{-1}$ [TOF (h^{-1})] and finally the reference for each phosphine.

The results in the two tables show that the hydrogenation of styrene or 1-hexene give the reduced products in rather good yields, and moderate TOF (except for the hydrogenation of styrene with TPPMS – Table 3, entry 1-that gives a very low TOF of 3 h^{-1}).

Table 1
Hydroformylation of 1-octene in an aqueous/organic two-phase system

Entry	Phosphine	Catalyst precursor	Catalyst (mol%)	Phosphine/Catalyst	PH_2/CO (bar)	T (°C)	t (h)	Conversion (%)	Selectivity (%)	n/i	TOF (h^{-1})	Ref.
1	**1** ($n=3$)	$[Rh(acac)(CO)_2]$	0.2	10	20	120	6	100	85	8	71	[20]
2	**1** ($n=6$)	$[Rh(acac)(CO)_2]$	0.2	10	20	120	6	100	88	9.5	73	[20]
3	TPPTS	$[Rh(acac)(CO)_2]$	0.2	10	20	120	6	100	78	3.6	65	[20]
4	**1** ($n=10$)	$[Rh(acac)(CO)_2]$	0.2	5	15	120	1	100	80	4.5	400	[21]
5	TPPTS	$[Rh(acac)(CO)_2]$	0.2	5	15	120	1	100	29	3.2	145	[21]
6	DPPETS	$[Rh(acac)(CO)_2]$	0.2	3	14	120	15	100	22	3.2	7	[22]
7	POP	$[Rh(acac)(CO)_2]$	0.02	10	20	80	21	67	100	7.5	160	[40]
8	POPam **17**	$[Rh(acac)(CO)_2]$	0.02	10	20	80	21	72	100	7.3	171	[40]
9	Xantphos	$[Rh(acac)(CO)_2]$	0.02	10	20	80	24	62	96	46	124	[40]
10	Xantham **18**	$[Rh(acac)(CO)_2]$	0.02	10	20	80	24	68	96	49	136	[40]
11	PAA-PNH	$[Rh(acac)(CO)_2]$	1	3	40	60	6	100	100	3	17	[54]
12	**30** and **31**	$[Rh(COD)_2][BF_4]$	0.03	1	100	60	18	99	99	3.1	182	[57]
13	**32a**	$[Rh(OAc)_3]_2$	0.1	10	25	125	2	95	100	2.4	475	[59]

Table 2
Hydroformylation of 1-hexene

Entry	Phosphine	Catalyst precursor	Catalyst (mol%)	Phosphine/catalyst	PH_2/CO (bar)	T (°C)	t (h)	Conversion (%)	Selectivity (%)	n/i	TOF (h^{-1})	Ref.
1	Sulphos	$[Rh(COD)(sulphos)]^+$	1	–	30	80	5	76	28	0.42	4	[24]
2	**10**	$[Rh(H)(CO)(PPh_3)_3]$	0.03	5	19	120	48	13	100	35	9	[34]
3	Amphos	$[\{RhCl(NBD)\}_2]$	0.4	3	40	90	24	99	96	1.7	10	[36]
4	Xantham **18**	$[Rh(acac)(CO)_2]$	0.02	10	20	80	24	71	96	48	142	[40]
5	N3P	$[Rh(acac)(CO)_2]$	0.1	10	20	80	16	32	100	2.8	20	[41]
6	**24** X = Na	$[Rh(acac)(CO)_2]$	0.1	11	10	80	4	92	94	2.4	216	[50]
7	PAA-PNH	$[Rh(acac)(CO)_2]$	0.4	4	40	60	20	100	100	2.2	13	[54]

Table 3
Hydrogenation of styrene in an aqueous/organic two-phase system

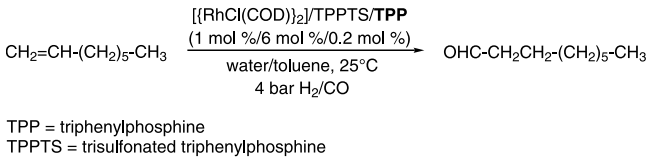
Entry	Phosphine	Catalyst precursor	Catalyst (mol%)	Phosphine/catalyst	PH_2 (bar)	T (°C)	t (h)	Conversion (%)	TOF (h^{-1})	Ref.
1	TPPMS	$[Ru(Cl)(H)(CO)(TPPMS)_3].3H_2O$	2	–	70	100	16	86	3	[6]
2	Sulphos	$[Rh(CO)_2(Sulphos)]^+$	0.2	–	30	65	5	100	100	[24]
3	Amphos	$[\{RhCl(NBD)\}_2]$	0.1	2	3	25	6	100	167	[36]

Table 4
Hydrogenation of 1-hexene in an aqueous/organic two-phase system

Entry	Phosphine	Catalyst precursor	Catalyst (mol%)	Phosphine/catalyst	PH_2 (bar)	T (°C)	t (h)	Conversion (%)	TOF (h^{-1})	Ref.
1	Amphos	$[\{RhCl(NBD)\}_2]$	0.1	2	3	25	6	100	167	[36]
2	**24** X = H	$[Rh(acac)(CO)_2]$	0.1	11	10	80	4	99	248	[50]

2. Thermoregulated phase-transfer phosphines

As seen previously, the main disadvantage of homogeneous catalysis (the separation of the product from the catalyst) can be swept away by performing the reactions in aqueous/organic biphasic systems, which enables the separation of the product from the catalyst into the two different phases and, following a simple decantation at the end of the reaction, enables immediate re-use of the catalyst solution. However, this approach is worthwhile only for precise substrates. If we want to generalise the reactions of hydrogenation, hydroformylation or carbon–carbon coupling reactions in two-phase systems, the reaction rates are lower than those found for monophasic catalysis [29,79] and the better recovery of the catalyst does not always compensate for the lower rates. The use of water as a second phase has, indeed, its limitations, especially when the water-solubility of the starting materials is too low, preventing adequate transfer of the organic substrate into the aqueous phase or at the phase boundary and consequently reducing the reaction rates. Cases like that can be dealt with by introducing a surfactant (or by using ligands that confer surfactant properties) or by adding a solvating agent or perhaps using a co-solvent. Those measures increase either the mutual solubility of the components or the mobility across the phase boundaries. However, from an engineering and economic standpoint, it is also important to remember that any 'foreign additive' will increase the difficulty and the cost of the purification step and, therefore, will decrease the interest of the two-phase catalysis in its purest form Chaudhari et al. [79] were the firsts to suggest introducing 'promoter ligands' that are soluble exclusively in the organic phase, thus modifying the solubility of the complex internally. By adding triphenylphosphine (TPP), which is soluble in organic solvents, to a rhodium complex containing the water-soluble ligand TPPTS, they increase the rate of the hydroformylation of the extremely water-insoluble 1-octene by a factor of 10–50 (Eq. (32)). During the reaction, there is a ligand exchange that leads to the formation of mixed-ligand complexes of the type $[Rh(H)(CO)(TPPTS)_{3-x}(TPP)_x]$, which contain the two types of ligands, ligands soluble in organic solvents (TPP) and water-soluble ligands (TPPTS).

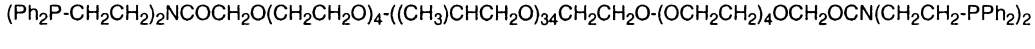


(32)

However, it is noteworthy that to develop this process industrially, addition of a 'promoter ligand' raises, once again, the problem of a 'foreign substance' with the resulting need for a costly separation step.

The problem of a 'foreign additive' is avoided in an approach discovered by Bergbreiter et al. [80] They applied the designation 'smart ligand' in describing the derivatives of ethylene oxide–propylene oxide–ethylene oxide triblock co-oligomers **46** and **47** (Fig. 26) that, together with rhodium precursors, form the complexes with a structure of the type $[Rh(\mathbf{46})_2][CF_3SO_3]$ or $[RhCl(\mathbf{47})_{1.5}]$.

The oligomers 46 and 47 possess the unusual property of undergoing a temperature-dependent phase change wherein they dissolve in water on cooling and phase separate from the aqueous systems on heating above the critical temperature cloud point (Cpt). Indeed poly(acrylamides) or poly(alkene oxides) can precipitate or phase-separate from water on heating and redissolve on cooling. One of the explanations of this phenomenon is the cleavage of the hydrogen bonds between the poly(ether) chains and water on heating. The rhodium complexes of the phosphines **46** or **47** as ligands ([Rh]/**46** and [Rh]/**47**) also possess the property of inverse temperature-dependent solubility in water associated with the ligands and the Cpts of the two rhodium complexes are below 25 °C. Those two complexes have been tested as catalysts for the hydrogenation of allyl alcohol in aqueous solvents (Eq. (33)). While the hydrogenation at 0 °C proceeds at an average rate, it is the behaviour of the catalysts on heating that is striking. On heating the samples to 40–50 °C, the reaction nearly stops. Although normal Arrhenius-type kinetics suggest that this temperature change should lead to a reaction occurring ca. 20-fold faster, the reaction rate decreases by a factor of 20 or more. This ca. 400-fold change in rate is due to the solubility changes that the complexes experience on heating. This effect is reversed on cooling to 0 °C, where the ligands are rehydrated and where the catalysts redissolve.



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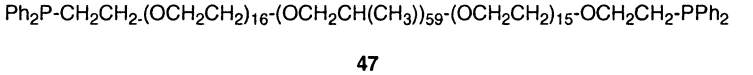
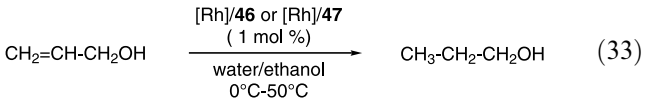


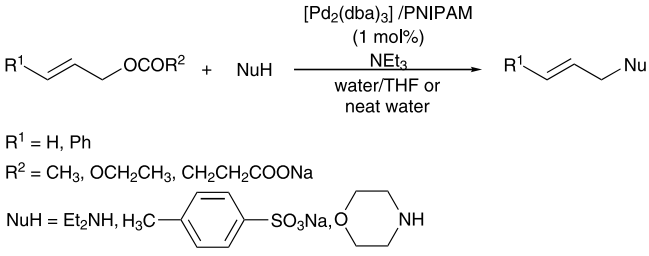
47

Fig. 26. Bergbreiter's 'smart' ligands.

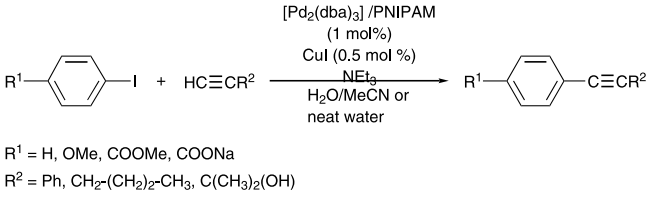


(33)

The polymer-bound palladium(0)-phosphine catalyst based on water-soluble polymer poly(*N*-*iso*propyl)acrylamide (PNIPAM **48**) (Fig. 27) takes advantages of similar effects [81]. With $[Pd_2(dba)_3]$ (dba = dibenzylidene acetone) and PNIPAM, a ligand exchange occurs to form the corresponding PNIPAM-bound Pd(0) catalyst. In water, it displays allylic substitution reactions (Eq. (34)) and cross-coupling reactions of terminal alkynes with aryl iodides (Eq. (35)) in good yields (86–96%). The recycling of the catalyst proceeds by heating above the PNIPAM's Cpt or by precipitating by adding hexane to the reaction mixture.



(34)

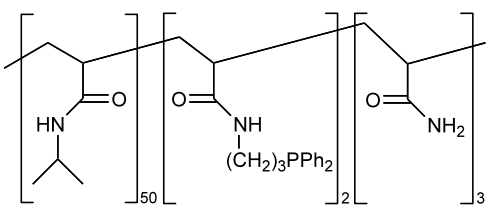


(35)

Then, Jin et al. have studied the properties of poly(ethylene oxide)-substituted triphenylphosphines PEOTPPs **49** (Fig. 28) [82].

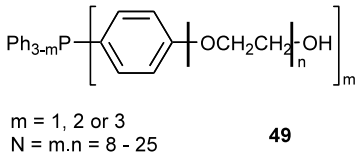
It has been shown that the PEOTPPs are completely soluble in water when (m.n) ≥ 8. Furthermore, their solubility in water can be controlled by varying the chain length.

With their poly(ethylene oxide)-substituted chains, the PEOTPPs possess, as expected, the property of inverse temperature-dependent solubility in water with a Cpt which is, for the different PEOTPPs, in the range



48

Fig. 27. The polymer poly(*N*-isopropyl)acrylamide (PNIPAM).



m = 1, 2 or 3
N = m.n = 8 - 25 **49**

Fig. 28. The poly(ethylene oxide)-substituted triphenylphosphines PEOTPPs.

from 26 to 95 °C. On the other hand, the solubility of poly(ether)-substituted compounds in some nonpolar aprotic solvents, such as toluene and heptane, increases with increasing the temperature.

The two properties described above enable transition metal complexes containing the poly(ethylene oxide)-substituted ligands to be designed into water-soluble catalysts possessing a thermoregulated phase-transfer function in the aqueous/organic two-phase system. The reaction is conducted as shown in Fig. 29. Before the reaction, the catalyst resides in the aqueous phase and the substrate in the organic phase. By heating above the temperature cloud point of the complex the catalyst can transfer into the organic phase to catalyse the reaction. Once the reaction is finished, the reaction mixture is cooled so that the catalyst returns to the aqueous phase to be separated from the product.

Thus, the phosphines PEOTPP combined with the rhodium precursor $[Rh(acac)(CO)_2]$ have been tested for the two-phase (water/heptane) hydroformylation of higher olefins such as 1-hexene, 1-octene, 1-decene or 1-dodecene. The process of the thermoregulated phase-transfer hydroformylation is as follows. At room temperature, almost all the Rh-PEOTPP catalyst remains in the aqueous phase. On heating to a temperature higher than Cpt, the catalyst precipitates from water and transfers into heptane where it transforms olefins into aldehydes. After hydroformylation is complete and the system is cooled to room temperature, the catalyst returns to water. Thus, a simple phase separation enables the continuous re-use of the catalyst.

The PEOTPP-Rh catalysts exhibit very good catalytic properties towards the hydroformylation of higher olefins in water/heptane. The best results were obtained in the presence of the phosphine with $N = 25$, $m = 1$, $[Rh(acac)(CO)_2]/PEOTPP = 0.1/1.2$ mol.%, at 100 °C, $PH_2/CO = 50$ bar for 5 h. Under these conditions, the hydroformylation of 1-hexene, 1-octene, 1-decene and 1-dodecene show similar results: a conversion of 95%, a selectivity in aldehydes of 90%, a normal/*iso* ratio of 1.8 and a TOF of 180 h^{-1}. Moreover, the catalysts can be re-used more than four times without any appreciable loss in activity and selectivity.

The application of thermoregulated phase-transfer catalysis (TRPTC) has been extended to the hydroformylation of styrene. Under the same catalytic conditions as previously, the activity of the phosphine PEOTPP

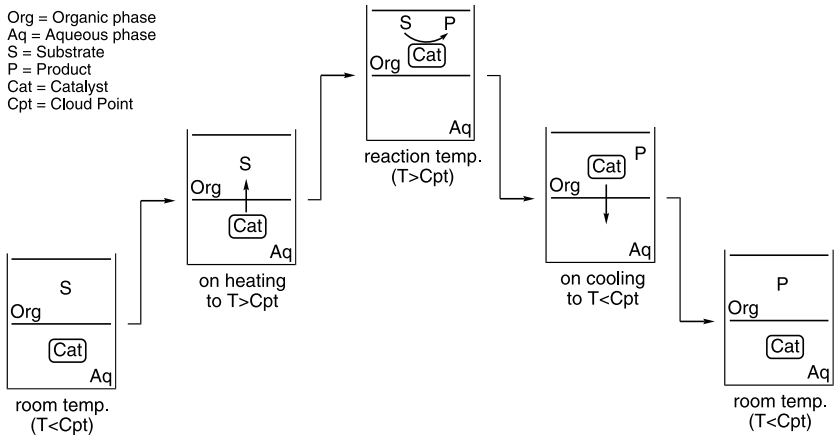


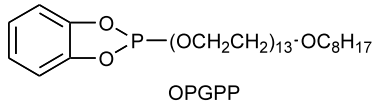
Fig. 29. The principle of the thermoregulated phase-transfer catalysis (TRPTC).

with $N = 25$ and $m = 1$ has been compared with TPPMS and TPPTS (Table 5). PEOTPP shows higher activity than the two sulfonated phosphines, however, Jin et al. designed the octylpoly(glycol)-phenylene-phosphite (OPGPP **50**) (Fig. 30), which shows even greater activity than PEOTPP [83].

Phosphines possessing the property of thermoregulated phase-transfer function, mainly poly(ethylene oxide) derivatives, confer the same property to the complexes to which they are coordinated. Thus, these complexes are designed for TRPTC. The process of TRPTC combines the advantages of the biphasic catalysis with the advantages of the monophasic catalysis. Indeed, at low temperature the catalyst and product are separated into two separate phases. Further, in comparison with the aqueous/organic two-phase catalysis, the process of TRPTC is more 'homogeneous' to some extent because the substrates and catalyst remain in the same organic phase at the reaction temperature and thus, can provide higher yields than the classical biphasic catalytic reactions.

Table 5
Activity of water-soluble phosphines for the hydroformylation of styrene with $[Rh(acac)(CO)_2]$ in water/heptane

	Conversion (%)	Selectivity in aldehyde (%)	Iso/normal
PETPP	95.7	92.8	2.2
TPPMS	87.0	83.0	1.5
TPPTS	37.8	36.9	2.8
OPGPP	99.2	99.0	4.9



OPGPP

50

Fig. 30. The thermoregulated phase-transfer phosphine OPGPP.

3. Literature update to 2001

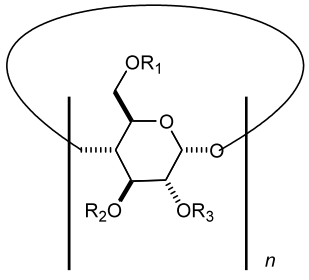
The following section updates this review to the end of 2001 and just into 2002 in some cases.

3.1. Phosphines containing sulfonated groups

Kohlpainter et al. [84] have reported the recent developments on the Ruhrchemie/Rhône–Poulenc oxo process. This process, based on the use of Rh/TPPTS, has been used commercially for hydroformylation since 1984.

Synthetic procedures for the sulfonated phosphines are cumbersome and difficult to reproduce because of the formation of phosphine oxide during the reaction. A new way of synthesising TPPDS straightforwardly, quickly and reliably has been proposed by Thorpe et al. [85]. Another approach was also reported for selective and oxide-free sulfonation of arylphosphines [86].

Owing to the low water solubility of higher olefins, viable hydroformylation rates can only be obtained by using surface-active ligands or mass-transfer promoters. In this context, Mathivet et al. [87] have proposed the use of chemically modified β-cyclodextrins, CyDs **51** (Fig. 31) to improve the mass transfer between the organic and aqueous phases. By adding **51** to a

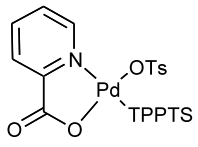


n = 6, 7, 8

R = alkyl, aryl, hydroxypropyl, H

51

Fig. 31. Chemically modified cyclodextrin.



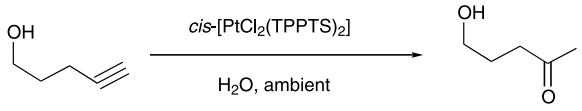
52

Fig. 32. Pd(II) complex of picolinate anion bound to TPPTS.

[Rh(acac)(CO)$_2$]/TPPTS system, the rate of hydroformylation of 1-decene improved dramatically.

Another way of improving the rates of biphasic hydroformylation of higher olefins is the use of microemulsions, which are an excellent tool for the solubilisation of oil (alkenes) in water (or other polar media) [88].

Further studies have been performed on catalysts with TPPTS or TPPM ligands, for example using iridium as the metal [89]. Several new uses have been reported for biphasic catalytic reactions with TPPTS. The complex *cis*-[PtCl$_2$(TPPTS)$_2$], prepared in water, has been used for the Markovnikov hydration of alkynes to ketones in water (Eq. (36)) [90].



(36)

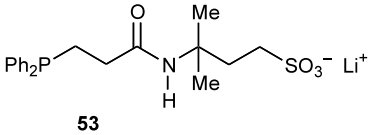
Dupuis et al. [91] have reported the Suzuki cross-coupling of arylbromides carried out with the water-soluble catalyst Pd/TPPTS in acetonitrile/water.

New catalysts have also been developed with TPPTS and TPPMS. The water-soluble analogue of Vaska's complex, namely *trans*-[IrCl(CO)(TPPMS)$_2$], exhibited good activity in the hydrogenation of olefinic double bonds in short-chain, unsaturated acids in aqueous solution, and for the hydrogenation and isomerisation of unsaturated fatty acids [92].

The Rh/TPPTS catalyst has its limitations, e.g. in water the catalyst system is only applicable to the hydroformylation of terminal olefins. However, with dicobalt octacarbonyl, TPPTS catalysed the hydroformylation of internal olefins in water/anisole [93].

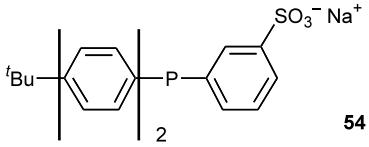
A new water-soluble catalyst [Pd(Pyca)(TPPTS)](TsO) (Pyca = pyridine-2-carboxylato, **52**) (Fig. 32) has been synthesised by Jayasree et al. [94] and shows good catalytic activity and selectivity in the carbonylation of styrene.

The phosphine PNS **53** (Fig. 33) has been developed by Ziolkowski et al. [95] and, in conjunction with



53

Fig. 33. The sulfonated phosphine PNS.



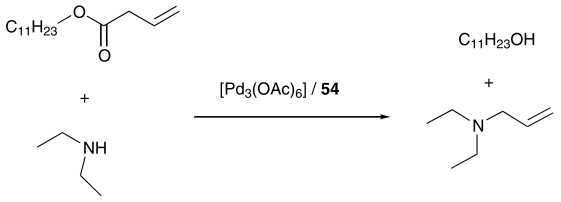
54

Fig. 34. Sulfonated phosphine.

[Rh(acac)(CO)$_2$], exhibited good activity in the hydroformylation and hydrogenation of C$_4$-unsaturated alcohols in water [96]. It was also used for the carbonylation of benzyl bromide to phenylacetic acid with [PdCl$_2$(COD)] in water/toluene [97].

New sulfonated phosphines have also been developed, such as $Ph_2P(CH_2)_4SO^{3-}\ K^+$. This ligand, combined with palladium, is an excellent precursor for the catalytic coupling reactions of aryl halides with arylboronic acid in toluene/water/ethanol [98].

Caron et al. [99] reported an efficient and simple synthesis of the amphiphilic phosphine **54** (Fig. 34). The catalytic activity obtained with this phosphine in the palladium-catalysed cleavage of undecyl allyl carbonate (Eq. (37)) was even higher than that observed with TPPTS.



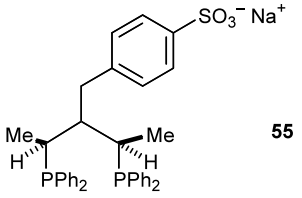
(37)

The diphosphine $BPDBzPSO_3^-\ Na^+$ **55** (Fig. 35) has been employed, in combination with Rh(I) and Ir(I), in a variety of aqueous/organic biphase asymmetric hydrogenations [100].

3.2. Phosphines functionalised with ammonium groups

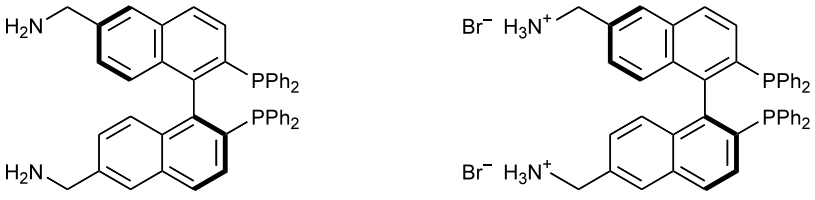
Among the recent developments in amphiphilic phosphines, new uses of the phosphine PTA have been reported. For example, the complex [RuCl$_2$(PTA)$_4$] actively catalysed the hydrogenation of CO_2 in aqueous solution [101].

Another ligand used in a new catalytic process is the diphosphine **57** derived from diam-BINAP **56** (Fig. 36) [102,103] which, with [Ru(η^3-2-methylallyl)$_2$(η^2-COD)] hydrogenated ethyl acetoacetate in water.



55

Fig. 35. The diphosphine BPD.



56 57

Fig. 36. Dicationic phosphine **57** ad its BINAP precursor **56.**

3.3. Phosphonated phosphines

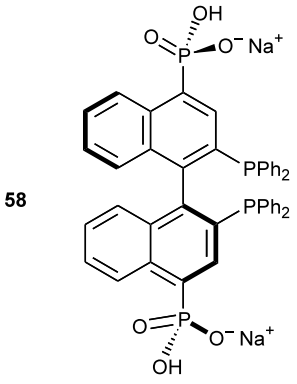
The water-soluble phosphonate-functionalised phosphine ligand $[Ph_2P(CH_2)_{12}PO_3]Na_2$ was prepared and reacts with $[Rh(COD)Cl]_2$ in methanol to give the complex $[Rh(COD)\{Ph_2P(CH_2)_{12}PO_3\}]Na_2$ [21]. This phosphine was also combined with $[Rh(COD)_2](BF_4)$ to give an active catalyst for the hydrogenation of decene in an aqueous emulsion [104].

The synthesis of new phosphonated phosphines $[Ph_2P(CH_2)_mPO_3]Na_2$ ($m = 2$, 6, 10, 12) has been reported by Bischoff et al. [105]. Their rhodium catalysts showed, in the two-phase hydroformylation of propylene, activities and selectivities similar to those obtained with Rh/TPPTS catalysts.

The ligand BINAP is widely used in asymmetric hydrogenation. Previous sections have described its use in its sulfonated or ammonium salt forms in biphasic catalysis. It is also possible to proceed to the phosphorylation of the BINAP ligand **58** (Fig. 37), [106] and with sodium precursors, it gives a very active system for the asymmetric hydroformylation of styrene and vinylacetate in water/ethanol mixtures.

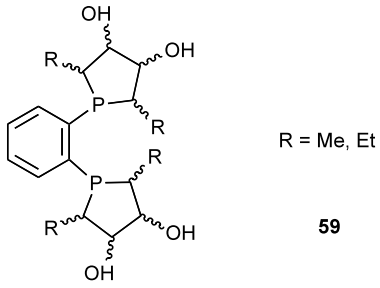
3.4. Phosphines with hydroxy groups

The synthesis of new polyhydroxy bis(phospholanes) **59** (Fig. 38) has been reported by Rajan Babu et al. [107]. The cationic rhodium complexes of these ligands have been found to be excellent catalysts for organic and aqueous phase hydrogenation of dehydroamino acids.



58

Fig. 37. BINAP-derived phosphonated phosphine.



R = Me, Et

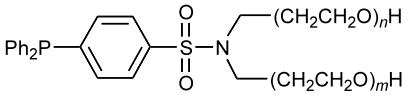
59

Fig. 38. Polyhydroxy bisphospholanes.

3.5. Thermoregulated phase-transfer phosphines

A novel water-soluble phosphine PEO–DPPSA **60** (Fig. 39) which possesses the property of inverse temperature–dependent solubility in water, has been synthesised by Jin et al. [108]. The rhodium complex of this phosphine ($RhCl_3 \cdot 3H_2O$/PEO–DPPSA) exhibits high catalytic activity in the aqueous–organic biphasic hydroformylation of 1-decene [25]. A ruthenium complex of PEO–DPPSA $[Ru_3(CO)_g(PEO–DPPSA)_3]$ was also investigated and was found to be very active for the aqueous–organic two-phase co-selective reduction of nitroarenes [109].

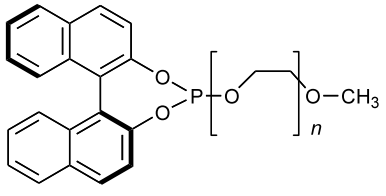
Another kind of ligand possessing the property of inverse temperature-dependent solubility in water is the phosphite **61** (Fig. 40) synthesised by Breuzand et al. [110]. This ligand was combined with $[Rh(COD)_2](BF_4)$ and the system showed high activity, chemo- and regio-



n + m = 17, 25, 34

60

Fig. 39. The water-soluble phosphine PEO-DPPSA.



n = 16-17

61

Fig. 40. Amphiphilic phosphite.

selectivity for the catalytic hydroformylation of styrene under thermoregulated, phase-transfer conditions.

4. Conclusion

One of the methods to solve the main problem of homogeneous catalysis, which is the separation and recycling of the catalyst, is to partition the catalyst and the product into two separate and immiscible phases, i.e. two-phase catalysis. However, in a system containing two liquid phases, mass transfer control is likely to dominate, which contrasts with the homogeneous system where kinetic control is operative. For the substrates with poor water-solubility, difficulty could be much more outstanding. The strategy of the TRPTC, in which the catalyst transfers into the organic phase to catalyse the reaction at higher temperature and returns to aqueous phase to be separated from the product at lower temperature, provides a potential solution to this problem. Thus, a large variety of catalytic reactions, from the carbon–carbon or carbon–nitrogen couplings to the hydrogenation, could be adapted, with suitable ligands, to TRPTC.

Acknowledgements

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