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New directions in water soluble homogeneous catalysis

Brian E. Hanson *

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg VA 24061-0212, USA

Contents

Abstract

A brief review of the role of water soluble ligands in the immobilization of homogeneous catalysts is given. Amphiphilic water soluble phosphines that aggregate in water are described. In aqueous biphasic catalysis use of the amphiphilic ligands leads to improved reaction rates with substrates that are poorly water soluble. The amphiphilic ligands

* Tel.: + 1-540-231-7206; fax: + 1-540-231-3255.
E-mail address: hanson@vt.edu (B.E. Hanson)

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aggregate in aqueous solution and there is evidence that these ligand aggregates solubilize the substrates in the aqueous phase.

Keywords: Homogeneous catalysis; Amphiphilic water soluble phosphines; Ligands

1. Introduction

The separation of catalyst and products remains an obstacle for the commercialization of homogeneous catalytic processes. Since immobilization of catalysts is an important process design feature there continues to be substantial research in the area. It can be argued though that many homogeneous processes, as practised industrially, use immobilized homogeneous catalysts [1]. Two well known examples illustrate this point. First the Union Carbide process which favors the hydroformylation of propene. The solvent in this case is a high boiling organic liquid comprised of aldol condensation products. Reactants and products are all gases at the operating conditions of the process thus the reaction engineering required to operate the process is much like that of a fixed bed reactor [2]. In the now abandoned Monsanto process for the asymmetric hydrogenation of pre-DOPA, an acetoamidocinnamic acid derivative (Eq. (1)). The process was run in methanol and the hydrogenated product crystallized from the reaction mixture, in greater than 99% e.e., leaving behind a homogeneous solution of the catalyst [3]. The catalyst and products are in separate phases and the unit operation for separation is a simple filtration. This route was abandoned not because of any fault in the asymmetric hydrogenation step or subsequent separation but rather because the precursor, pre-DOPA is too expensive, and access to the process is no longer protected by patents.

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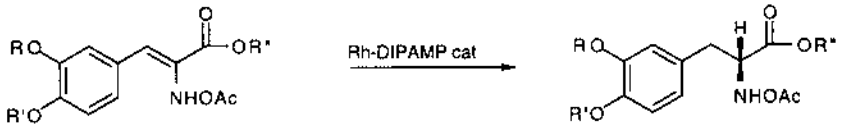

pre-DOPA

Significantly these 'immobilized catalysts' do not involve solids. A more recent example of catalyst immobilization is the biphasic approach [4]. It is argued that the problems associated with catalyst leaching and ligand degradation add more costs to a process in recovery and recycling than is saved in process simplification. The biphasic approach is seen as superior to immobilization on solids and indeed it has proven very successful in the Ruhrchemie/Rhone Poulenc process for the hydroformylation of olefins [4].

As new homogeneous processes are developed the issue of product separation from the catalyst must be solved in an economically viable way for the process to succeed. As details emerge from the recently developed metolachlor synthesis over a homogeneous iridium/ferrocenylphosphine catalyst it will be interesting to see

how the catalyst separation issue is addressed (Eq. (2)) [5]. One possibility is that a heterogeneous version of the catalyst is employed [5d]. From past experience the method to be used for separation is likely to be unique to the specific chemical process.

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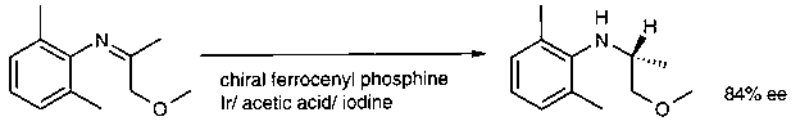


metolachlor synthesis

2. Catalyst immobilization

A brief review of immobilization methods is given in this section. Immobilization is meant in its broadest sense i.e. any means for the effective control and recovery of the catalytically active species. The section emphasizes recent examples on the use of solids, polymers, and the biphasic approach to immobilization.

2.1. Immobilization on solids

Supported liquid phase catalysis was devised as a method for the immobilization of homogeneous catalysts on solids [6]. When the liquid phase is water for example, a water soluble catalyst may be physically bound to the solid. Supported aqueous phase rhodium/TPPTS hydroformylation catalysts show excellent rate enhancements for water insoluble substrates [7,8]. This is attributed to the increased surface area between the aqueous phase which is supported and the substrate phase. Reaction selectivity however often decreases. This may be due to the fact that the reaction environment is not bulk water but rather the water-organic interphase region. Supported aqueous phase palladium/TPPTS complexes are extremely active and selective for certain alkylation reactions [9].

The pores of zeolites provide a highly ordered space for catalysis and zeolites themselves are excellent catalysts for a variety of reactions. As a support for homogeneous catalysts zeolites offer the possibility not only of immobilizing metal complexes but also to influence reaction selectivity based on the size of pores which give access to the intrazeolitic space. This method of immobilization is best illustrated by the ship-in-a-bottle technique in which a metal complex is synthesized inside a zeolite cage and is too large to pass out of the zeolite through the smaller pores [10,11]. Catalysts of this type can direct the oxidation of alkanes toward the terminal carbon atoms rather than the more reactive internal positions [11].

The immobilization of catalysts on polymers continues to be an area of interest [12]. One of the more recent developments is to immobilize catalysts on polymers that have strongly temperature dependent solubilities [13]. An important design aspect of the soluble polymer bound catalysts is that the ligand serves as an end

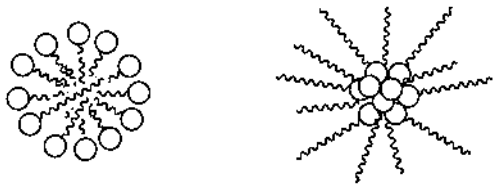


Fig. 1. Schematic representations of a micelle. Polar head groups directed out and a reverse micelle, polar head groups directed in.

group of the polymer; consequently it has little effect on the physical characteristics of the polymer [13b]. The most desirable case is for the polymer to be completely soluble at reaction temperature and completely insoluble at room temperature for reaction work up. Recently epoxidation catalysts have been bound to soluble polymer supports [14]. The polymer NAFION has a unique structure that has been compared to zeolites. Cationic complexes may be ion-exchanged on to NAFION for supported catalysis applications [15].

2.2. Immobilization via biphasic catalysis with amphiphilic ligands

The use of aqueous phase catalysis relies on highly water soluble ligands such as TPPTS [16] or BINAS [17] to keep the catalytically active metal in the aqueous phase. Ligand modification for improved activity has lead to the use of amphiphilic or tenside ligands in aqueous biphasic systems. A tenside ligand has one or more of the following properties, it may aggregate in solution to form micelles, they partition to the air | liquid, liquid | liquid or solid | liquid interfaces, or it may act as a solubilizing agent. Water dispersible tensides are characterized by the presence of a strongly hydrophilic region of the molecule and a large hydrophobic region. In water the hydrophobic regions are forced to cluster together so as to not disrupt the strong hydrogen bonding interactions in the aqueous phase. This net result is the formation of micelles. Some tensides may be dispersed in a nonaqueous phase to give reverse micelles. In this case small amounts of water typically are present to stabilize the hydrophilic core. Idealized representations of micelles are shown in Fig. 1.

The possibilities for a tenside ligand can be represented by the placement of the donor atom relative to the hydrophobic and hydrophilic regions of the molecule (Fig. 2). Most tenside ligands however have geometries dictated by the nature of the donor atom which complicates this simple picture. In the case of

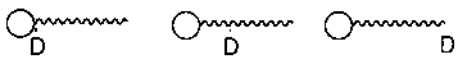


Fig. 2. The open circle represents the polar head group, D represents the donor atom.

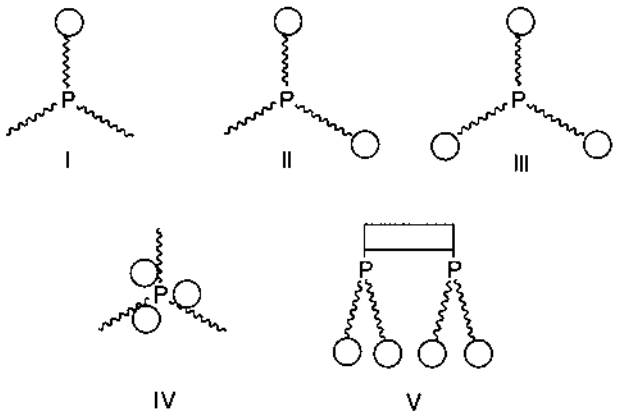


Fig. 3.

phosphines, including chelating phosphines, some of the possibilities are shown in Fig. 3.

The polar head group may be cationic, e.g. $-[NMe_3]^+$, $-[PMe_3]^+$; anionic, e.g., $-[CO_2]^-$, $-[SO_3]^-$, $-[PO_3]^{2-}$, or nonionic, e.g. $-(OCH_2CH_2)_n-OMe$. Specific examples of the types I–V are: I: $Ph_2P(CH_2)_3SO_3Na$ [18]; II: (menthyl)$P[(CH_2)_8C_6H_4SO_3Na]_2$ [19]; III: $P[(C_6H_4)(CH_2)_nC_6H_4SO_3Na]_3$ (**1**) [20]; IV: $P[C_5H_3N^+(CH_2)_2CH(SO_3^-)C_{12}H_{25}]_3$ [21] and V: (xanthene)$P_2[(C_6H_4)O-(CH_2)_6C_6H_4SO_3Na]_4$ (**2**) [22], and (binaphthyl)$P_2[(C_6H_4)(CH_2)_6C_6H_4SO_3Na]_4$ **3** [23]. See also Figs. 4 and 5 below. Tenside ligands have found application in biphasic

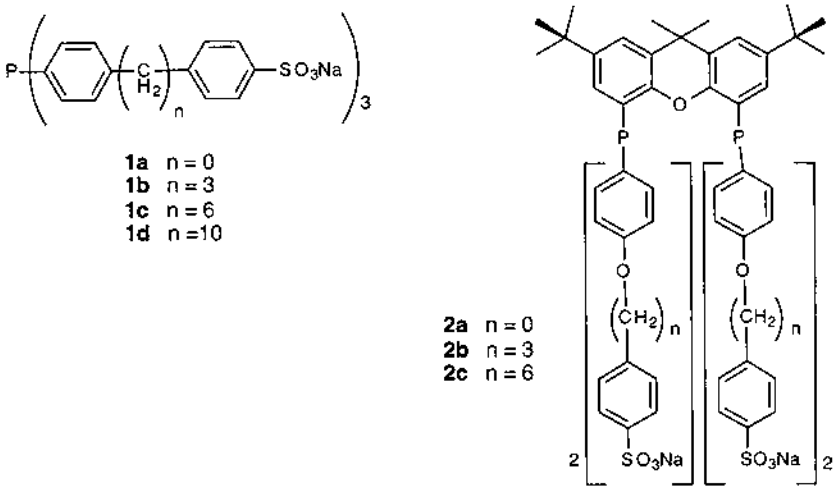


Fig. 4. Examples of amphiphillic ligands that have been shown to improve rates in two phase reactions.

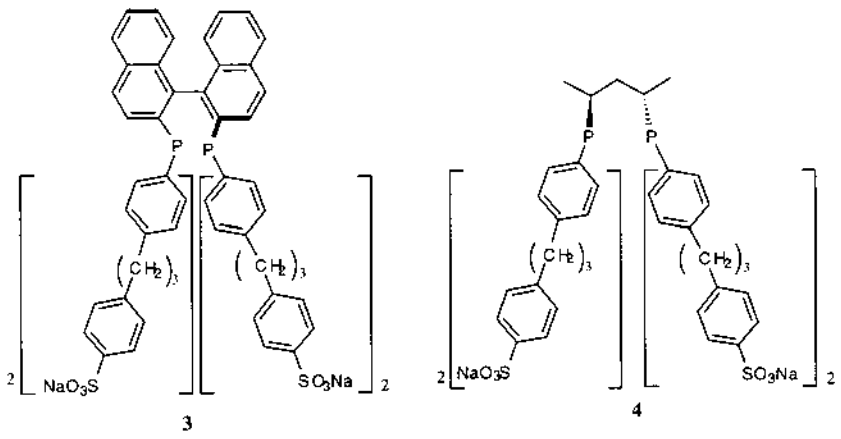


Fig. 5.

catalysis where they are observed to improve reaction rates for water insoluble substrates [24].

Tenside ligands may also be constructed to function with other solvent combinations, for example between a fluorocarbon phase and a hydrocarbon phase or between a fluorocarbon phase and water. Fluorinated sidechains added to ligands serve as the fluorophilic group in these ligands [25]. Fluorinated tensides may also act as solubilizers in supercritical CO_2 applications [26].

The geometric shape of phosphine amphiphiles (see Fig. 3) limits the way in which they may aggregate in micelles or vesicles. Nevertheless there is evidence that amphiphilic phosphines serve not only as solubilizers for substrates in the aqueous phase but also form micellar like aggregates and, in special cases, vesicles [22]. The trisulfonated ligands, **1** [20], have been shown to aggregate in water with diameters of up to 4.5 nm depending on the number of methylene groups that are present. The xantphos derivative, **2**, has recently been shown to form vesicles of up to 130 nm in diameter [22]. The presence of vesicles is demonstrated by observation of flattened spherical structures by electron microscopy in samples prepared by sonication followed by freeze fracture [22]. Importantly the amphiphilic phosphines show improved reaction rates in two phase applications compared to water soluble ligands which are not amphiphilic.

In addition to tenside ligands, surfactants may be added to otherwise water soluble (or insoluble) catalysts. The role of added surfactant may be to increase the rate or alter the reaction selectivity. For example enantioselectivites can be altered in micelles constructed of chiral surfactants [27]. When surfactants are added to hydroxy substituted chiral phosphines the increase in enantioselectivity can be substantial [28].

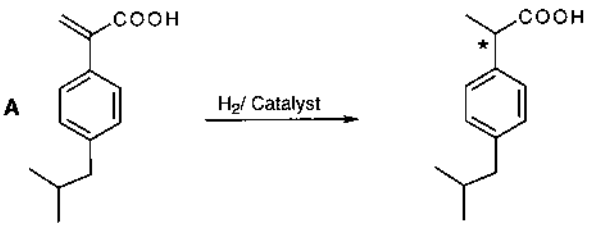
3. Recent examples of biphasic catalysis

Recently we prepared potentially surface active analogs of BINAP, **3** [23,29a], and BDPP, **4** [29b] (see Fig. 5). The ligands are similar in shape to the xantphos derivative, **2**; thus they are of type V described above. Tetrasulfonation occurs in sulfuric acid at room temperature. The mild conditions avoid sulfonation of the binaphthyl portion of the molecule and gives little oxidation. Sulfonation of BINAP, itself, requires high temperatures [30], and sulfonation of BDPP requires fuming sulfuric acid [31]; in both cases oxidation occurs.

3.1. Hydrogenation of prochiral 2-R-propenoic acids

The ligand, **3**, in combination with ruthenium was investigated in the asymmetric hydrogenation of the ibuprofen precursor, **A** [23,29a]. The catalytic reaction is shown in Eq. (3). The catalyst was prepared in situ from $[(C_6H_6)RuCl_2]_2$ and the diphosphine ligand. It has been shown by others that the reaction of BINAP with $[(C_6H_6)RuCl_2]_2$ leads to $(BINAP)RuCl_2$ [32]. The chloride may be further substituted by carboxylate.

(3)



Literature results for the hydrogenation of this substrate with ruthenium BINAP complexes prepared in situ gave up to 88% e.e with a catalyst concentration of ca. 4 mol% [32]. Under similar conditions at a catalyst concentration of 1 mol% we obtained an e.e. of 83% with BINAP as the ligand. The results of Ru/BINAP catalyzed hydrogenations of **A** are compared with the results obtained with ruthenium complexes of **3** in Table 1 below.

Table 1
Asymmetric Hydrogenation of **A**[a]

Catalyst	Subs	Subs/cat	Time/days	Solvent	Conversion/%	e.e./%
1. Ru/BINAP	A	100	0.75	MeOH	100	83
2. Ru/3	A	100	0.75	MeOH	65	66
3. Ru/3	A	100	2.5	MeOH	82	56
4. Ru/3	A	100	3.5	H_2O/EtOAc	100	19
5. Ru/BINAP*	B	50	3.5	H_2O/EtOAc	54	78

[a] Entries 1–4 from Ref. [29], Temp = 25°C, $P = 1000$ psig, conversion by NMR, e.e. by chiral HPLC. Catalysts were prepared in situ as described in the text. Entry 5 from Ref. [30], BINAP* = sulfonated BINAP, substrate = pro-naproxen propenoic acid derivative, Temp = 25°C, $P = 1380$ psig.

Table 2

Ligand[a]	Solvent	*P*/atm	Time/h	Yield/%	e.e./%
1. BDPP	MeOH	1	0.2	100	72
2. BDPPTS	MeOH	1	0.75	100	75
3. BDPPTS	EtOAc/H_2O	15	–	100	45
4. BDPPTS	EtOAc/H_2O	1	1.3	100	44
5. **4**	EtOAc/H_2O	1	1.5	100	69
6. **3**	EtOAc/H_2O	1	0.06	100	69

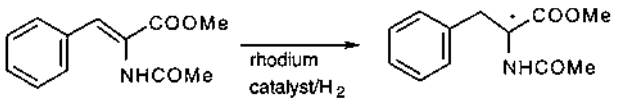
[a] Entries 1–5 from Ref. [29b], entry 6 from Ref. [29a].

Several interesting features are evident from the data. First enantioselectivity suffers with the new surface active BINAP derivative. This is true in methanol alone as the solvent but is more evident under biphasic conditions (H_2O/EtOAc). With the new catalysts enantioselectivity drops as conversion increases; this suggests that the product is racemized in the presence of the catalysts. Compared to the results in methanol the catalyst in water has a slightly lower activity and the longer reaction times lead to still lower enantioselectivities. Although a direct comparison is not possible because of different substrates it appears that the surface active phosphine **3** gives much higher rates than sulfonated BINAP (BINAP* in Table 1). At a lower pressure the apparent TOF is four times greater with **3** than with BINAP*, but the enantioselectivities are much lower. It is not clear at this time why the selectivities should be lower with **3.** One possibility is that ibuprofen, the product from hydrogenation of **A**, is more susceptible to racemization under the reaction conditions compared to naproxen, the hydrogenation product of **B**.

3.2. Hydrogenation of acetoamido cinnamic acid methyl esters

The hydrogenation of phenyl alanine precursors is an excellent test reaction for asymmetric hydrogenation reactions in water, see Eq. (4) [31]. Representative results obtained with rhodium complexes of **3** and **4** are compared with BDPPTS in Table 2. Fewer reaction conditions have been explored with these ligands due to the limited quantities of material. Two features are apparent from the data available. First the enantioselectivity observed with the surface active version of BDPP, namely **4**, under two phase reaction conditions is closer to that of BDPP or BDPPTS in methanol than BDPPTS in two phase conditions.

(4)

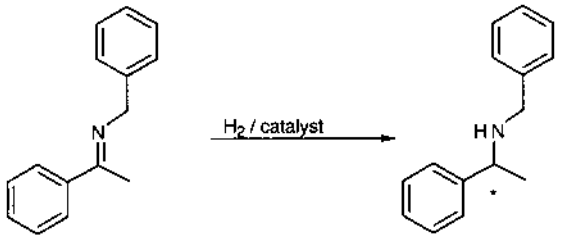


This suggests that the local environment is perhaps less polar in aqueous phase catalysts of **4** compared to BDPPTS. A much faster catalyst is obtained with **3** however the benchmark ligand for comparison, namely sufonated BINAP, has not been investigated in this reaction.

3.3. Hydrogenation of acetophenone N-benzylamine

Preliminary results show that the ligands **3** and **4** are effective for the biphasic hydrogenation of imines. As a test reaction the hydrogenation of acetophenone *N*-benzylamine was studied (Eq. (5)).

(5)



In this reaction the best results, with respect to rate and enantioselectivity, in the aqueous phase hydrogenation of acetophenone *N*-benzylamine have been reported with the monosulfonated version of BDPP. The tetrasulfonated ligand gives much lower enantioselectivity. The comparison available from experiments under the same two phase reaction conditions at the moment is between **3** and BDPPTS. Table 3 shows the results. The first entry for BDPPTS is comparable to those reported in the literature [33]. The ap1parent TOF doubles when the reaction is done with **3** but more significantly the enantioselectivity increases. The influence on reaction rate is attributed to the surface active character of **3**. Direct proof for the aggregation of **3** however has not yet been obtained although similarly shaped ligands do aggregate. Clearly more experiments are required to elucidate the factors that influence activity and selectivity.

3.4. Hydroformylation of olefins

The biphasic hydroformylation of olefins is a reaction of great commercial importance [4]. Industrial practice however is limited to lower olefins that have sufficient solubility in water to allow good reaction rates. With higher olefins biphasic processes provide an attractive solution to the separation problem but suffer from poor rates due to substrate insolubility. We have investigated many of

Table 3

Catalyst[a]	conversion/%	e.e./%
Rh-**3**	98	56
Rh-BDPPTS	48	29

[a] From Ref. [29a]. The reactions were done at 25°C, for 1.7 days under a pressure of 70 atm, conversion and enantiomeric excess were determined by NMR (2,2,2-trifluoro-1-(9-anthryl)ethanol as the shift reagent).

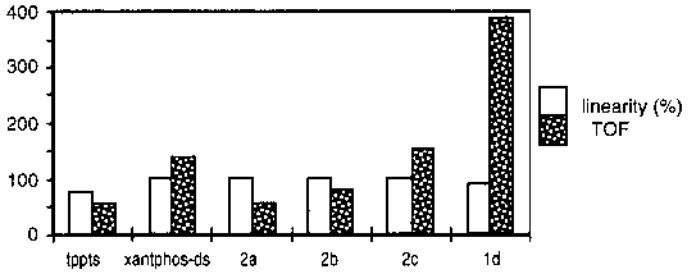
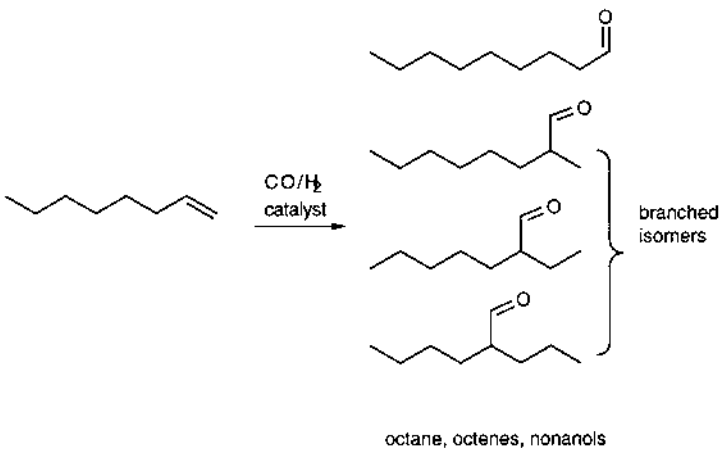


Fig. 6. Octene Hydroformylation with various ligands. Xantphos-ds = disulfonated xantphos [35] **1d**, as in Fig. 4 with $n = 10$, **2a**, **2b**, **2c**, as in Fig. 4 with $n = 0$, 3, 6 respectively. In all cases the ligand to rhodium ratio is 5, the reaction temperature is 120°C, and the substrate to rhodium ratio is 500. The biphasic solvent system in each case is MeOH + H_2O, 1/1 and the organic phase is olefin plus nonane.

the amphiphilic ligands mentioned above in the two phase hydroformylation of octene and tetradecene as test reactions for the carbonylation of higher olefins in water.

The possible reactions for the hydroformylation of 1-octene are given in Eq. (6). Ideally the hydroformylation of alpha olefins should be operated to maximize the yield of linear aldehyde. The possible byproducts include branched aldehydes, alcohols from hydrogenation of aldehydes, isomeric alkenes, and alkane from olefin hydrogenation.

(6)



Some of the results for octene and tetradecene hydroformylation are summarized in Figs. 6 and 7 respectively for ligands of the type **1**, and **2** above. The results shown were obtained in identical reactors, at the same stirring rate, temperature and pressure. The activities are expressed as average turnover frequencies (octene) or percent conversion (tetradecene). In this method of comparison the activity of the more active catalysts is under estimated since the rate in a batch reactor drops as the substrates are consumed. In all cases the substrate to catalyst ratio is 500 to 1.

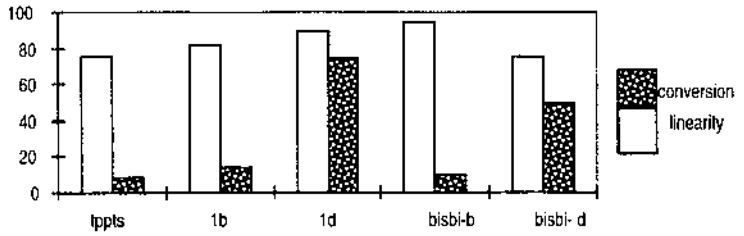


Fig. 7. Tetradecene hydroformylation. In all cases the ligand to rhodium ratio is 7:1; the substrate:rhodium ratio is 500:1; the reaction temperature is 120; the solvent is $MeOH + H_2O$; and the reaction time is 20 h. Bisbi-b and bisbi-d are (bisbi) $P_2[(C_6H_4)(CH_2)_nC_6H_4SO_3Na]_4$ where $n = 3$ and 10, respectively.

The results shown were obtained in 50% aqueous methanol. The substrate and products form a separate phase under these reaction conditions. Methanol does slightly improve the solubility of olefins in water however. Methanol also serves to destabilize any aggregates that may form. In spite of this the catalytic results are consistent with a solubilizing role for the amphiphilic phosphines. NMR measurements, light scattering experiments, and electron micrographs on suitably prepared samples show evidence of substrate solubilization [22,34]. Clearly the monodentate, micelle forming ligand **1d** shows the best reaction activity and the rigid chelating ligands of type **2** show the best selectivity. The tendency of the monodentate ligands to form small micellar aggregates, vide infra, may play a role in accelerating reaction rates.

4. Evidence for ligand aggregation

As mentioned above evidence for aggregation of the amphiphilic ligands comes from a variety of physical methods. Shown in Fig. 8 is the electrical conductivity

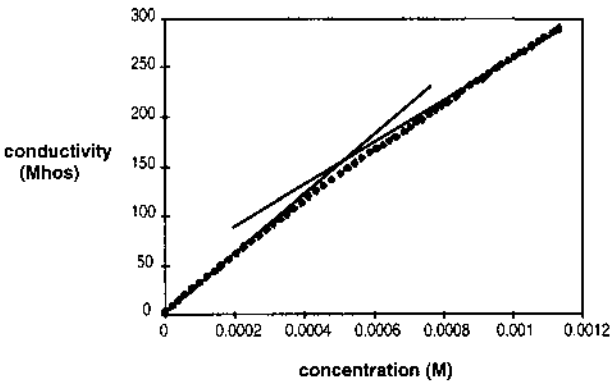


Fig. 8. The cmc of **1b** as determined by conductivity measurements is 4.7×10^{-4} M.

data for the ligand **1b**. The apparent cmc from this data is 4.8×10^{-4} M, similar values are obtained from pyrene and pyrene carboxaldehyde probe experiments [34]. The size of the aggregates as determined by dynamic light scattering, $d = 4.5$ nm suggests that only a small number of ligands cluster together, perhaps four to six ligands. In this respect the aggregates most closely resemble the bile salt micelles which can have very small aggregation numbers.

Dynamic light scattering on solutions of **2b** show evidence of much larger micelles, with diameters of up to 130 nm [22]. Structures of these dimensions are seen also by electron microscopy in samples prepared from solutions of **2b** [22]. Interestingly these structures grow in size in the presence of octene, a typical substrate for hydroformylation with these ligands. This lends support to the hypothesis that the role of amphiphilic ligands in promoting biphasic reactions is to increase the solubility of ligand in the catalyst phase.

5. New directions

Ligands, such as **2b**, that form vesicles, without the addition of emulsifier or cosurfactant, represent a new class of materials for catalysis. Further design and synthesis of this type of ligand will find application in two phase catalysis not only for rate enhancement but also for control of regioselectivity, and perhaps enantioselectivity as well, when the vesicle forming ligands are chiral.

Acknowledgements

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