

## Review article

# Film-shear reactors and more water-soluble ligands; new tools for doing inorganic and organometallic chemistry in aqueous solution

David R. Tyler

Department of Chemistry and Biochemistry, 1253 University of Oregon, Eugene, OR 97403, USA



## ARTICLE INFO

## Keywords:

Water-soluble phosphine ligands  
Catalytic hydration  
Film-shear reactor  
Acetone cyanohydrin  
Dihydrogen hydrogen bonding

## ABSTRACT

Four developments from the author's laboratory related to doing organometallic and inorganic chemistry in aqueous solution are reviewed. First, the development of new water-soluble cyclopentadienyl ligands and bidentate phosphine ligands is discussed. These ligands were developed because many of the standard water-solubilizing ligands contain  $-\text{SO}_3^-$  or  $-\text{OH}$  groups, which can bond to metal centers and thus inhibit catalysis. The new cyclopentadienyl ligands were used to generate water-soluble 19-electron complexes, and the water-soluble  $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3)_2$  ligand was used in a pressure-swing process to separate nitrogen from natural gas. Next, the catalytic hydration of nitriles, acetone cyanohydrin in particular, is discussed. The ability to catalytically hydrate acetone cyanohydrin (ACH) in aqueous solution would be particularly useful because ACH hydration is used in the preparation of methyl methacrylate and other methacrylates. The industrial method for hydrating ACH, known as the acetone cyanohydrin process, uses sulfuric acid and produces large amounts of by-product, which requires large amounts of energy to properly dispose of. An aqueous catalytic process could save energy and materials. Next, the use of a film-shear reactor for intimately mixing reactants in an aqueous solvent with reactants in an immiscible organic solvent is described. Finally, the inertness of the  $\eta^2\text{-H}_2$  ligand in water-soluble  $\text{Fe}(\eta^2\text{-H}_2)$  and  $\text{Ru}(\eta^2\text{-H}_2)$  complexes to substitution by water in aqueous solution is discussed. Surprisingly, the substitution by water is approximately thermochemically neutral so there is little driving force for the reaction. Dihydrogen hydrogen bonding may also contribute somewhat to the inertness.

## 1. Introduction

Organometallic chemists usually go to great lengths to remove water from their reaction systems because water has historically been considered a poison for organometallic reactions [1–3]. However, a report in 1962 detailing olefin hydrogenation in water using  $\text{Co}(\text{II})$  complexes [4] and a patent describing biphasic hydroformylation in 1976 [5,6] were early indicators that at least some organometallic reactions could be carried out successfully in the presence of water. This situation has changed dramatically over the past several decades, and numerous types of organometallic reactions can now be carried out in water or in mixed solvent systems containing some water [7–10]. After a brief introduction, this paper will discuss four aspects of aqueous organometallic and inorganic reaction systems investigated in our laboratory. In particular, because the insolubility of organometallic complexes in water is often the most important hurdle to overcome when doing aqueous organometallic chemistry, our development of new water-solubilizing cyclopentadienyl and phosphine ligands will be reviewed. Next, the catalytic hydration of nitriles, acetone cyanohydrin

in particular, will be discussed. A new microfluidics method for intimately mixing reactants in an aqueous solvent with reactants in an immiscible organic solvent using a film-shear reactor will then be described. To conclude, the peculiar inertness of  $\text{Fe}(\eta^2\text{-H}_2)$  and  $\text{Ru}(\eta^2\text{-H}_2)$  complexes to substitution by water in aqueous solution will be examined.

## 2. Properties of water relevant to organometallic chemistry

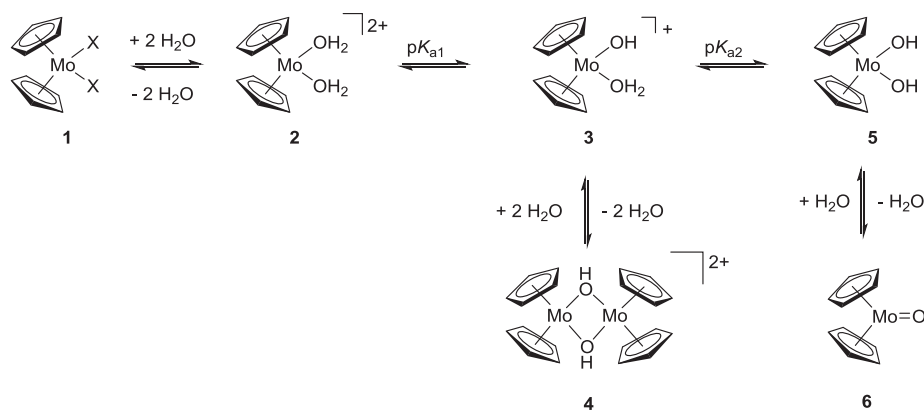
Water has many properties that make it a useful reaction solvent [11]. Among those properties are its low toxicity, low cost, low aroma, ready availability, non-flammability, and general overall safety – at least in comparison to many organic solvents [12]. In addition to these properties, its high polarity can be exploited for easier separations. It is noteworthy that the polarity of water decreases with increasing temperature. Thus, the solubility of typical organic molecules increases with the increasing temperature of water. This feature can be exploited for the separation of organic reaction products from a water-soluble catalyst by cooling the aqueous reaction solution. One final set of

E-mail address: [dt Tyler@uoregon.edu](mailto:dt Tyler@uoregon.edu).<https://doi.org/10.1016/j.ica.2018.10.003>

Received 30 May 2018; Received in revised form 28 September 2018; Accepted 1 October 2018

Available online 03 October 2018

0020-1693/ © 2018 Elsevier B.V. All rights reserved.



**Fig. 1.** Equilibria of the various molybdocene species present in an aqueous solution of  $[\text{Cp}_2\text{Mo}(\mu\text{-OH})]_2^{2+}$ . Note that the Cp-Mo ligation is stable in water.

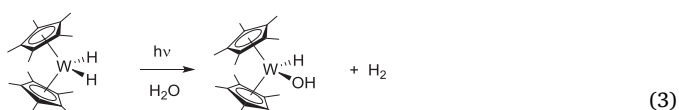
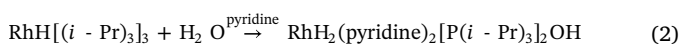
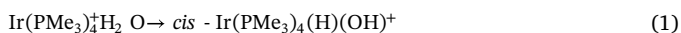
features is important to point out. Water has a high thermal conductivity, high heat capacity, and a high heat of evaporation [13]. In consequence, exothermic reactions can be controlled quite effectively if they are carried out in water.

### 3. Problems using organometallic complexes in water

Probably the most obvious problem when trying to do organometallic chemistry in water is that most organometallic complexes are not soluble in water. This problem is so significant that a subsequent section is devoted to discussing how to make organometallic complexes water-soluble. A second major problem in many systems is that intricate pH-dependent equilibria are common. An example of such equilibria from our study of the  $[\text{Cp}_2\text{Mo}(\mu\text{-OH})]_2^{2+}$  catalyst in aqueous solution is shown in Fig. 1 [14].

At the very least, these equilibria make mechanistic studies more difficult. The myriad of other problems with doing organometallic chemistry in water have been well reviewed [13] so other than to briefly mention them they will not be discussed in detail here. Among these other problems are 1) the susceptibility of metal-carbon bonds to electrophilic attack by water (e.g., Scheme 1); 2) ligands can react with water; 3) oxophilic metal centers can react with water; 4) some metal centers can be protonated by water; and 5) the hydride ligand in metal hydride complexes can react with water.

To conclude this section, it is noted that, although the oxidative addition of water is every chemist's ideal way to activate water, this reaction is infrequent. Several examples are shown in Eqs. (1)–(3) [15–18].



## 4. Water-solubilizing organometallic complexes

### 4.1. Water-solubilizing ligands

As mentioned above, the insolubility of many organometallic



**Scheme 1.** Metal-carbon bonds are susceptible to electrophilic attack by water.

complexes in water is a major obstacle for doing organometallic chemistry in water. Methods are needed therefore to make complexes water soluble. A standard method for making a water-insoluble organometallic complex water soluble is to use water-soluble ligands. Many early studies relied on the PTA ligand, THMP, and the sulfonated derivatives of  $\text{PPh}_3$  and its variants (Fig. 2) [19–21]. Homogeneous catalysts with ligands such as those in Fig. 2 have been used in numerous catalytic reactions [1,7,21–27].

### 4.2. Newer water-solubilizing ligands

Water-solubilizing functional groups other than  $-\text{SO}_3^-$  have also been used to render organometallic complexes water soluble. Three examples from our laboratory are shown in Fig. 3.

Complexes 1 uses  $-\text{COO}^-$  groups to solubilize the  $\text{Cp}_2\text{W}_2(\text{CO})_6$  dimer [28], and  $-\text{NH}_3^+$  groups water-solubilized the analogous  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  dimer (2) [29,30]. Both complexes were used to generate 19-electron complexes in aqueous solution (Scheme 2). The 19-electron complexes were used to reduce water-soluble substrates and electron-transfer “mediators” in hydrogen-producing reactions (Scheme 3).

The syntheses of several other unusual water-soluble ligands derived from the cyclopentadienyl ligand are shown in Scheme 4 [31].

### 4.3. Water-soluble bidentate phosphine ligands

Our more recent synthetic work has focused on the development of water-soluble bidentate phosphine ligands. Our reason for developing these ligands was that, in collaboration with Lyon and Miller at Bend Research, Inc., we were interested in using  $\text{Fe}(\text{bidentate phosphine})_2\text{X}_2$ -type complexes as scrubbers for removing  $\text{N}_2$  from natural gas in a pressure-swing process in aqueous solution (Scheme 5) [32–34].

Our results showed that ligands with  $-\text{SO}_3^-$  groups and  $-\text{OH}$  groups were not satisfactory because these groups coordinated to the metal and prevented the binding of  $\text{N}_2$ . An example of a hydroxy group bonding to the Fe center is shown in Fig. 4 [35].

Our solution to this problem was to use  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3$  as the R group on the bidentate phosphine ligands. The synthetic route is shown in Scheme 5, and the solubilities of various ligands in water are shown in Table 1 [35].

### 4.4. Other water-soluble ligands.

For completeness, it is noted that many other types of ligands can be water-solubilized using the functional groups discussed above. NHC ligands provide an example [36].

Download English Version:

<https://daneshyari.com/en/article/11009822>

Download Persian Version:

<https://daneshyari.com/article/11009822>

[Daneshyari.com](https://daneshyari.com)