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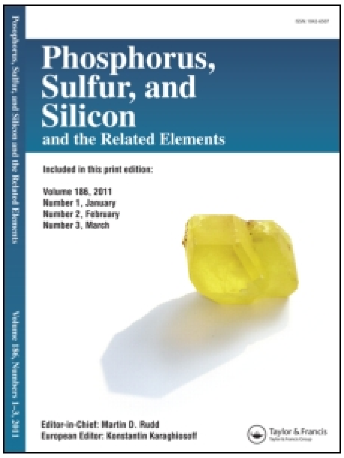

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Construction of Water-Soluble Phosphines, New Advances in Aqueous Organometallic Chemistry

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Interest in aqueous organometallic chemistry stems from the fact that water-soluble transition metal compounds have found applications as catalysts in commercially-viable industrial processes for bulk and fine chemicals synthesis and also for their continued utility in biomedicine. As a solvent, water is unique because it displays polar and protic properties. The strong propensity of water to involve in hydrogen bonding interactions and its ability to act as a donor ligand to transition metals makes it even more unique, non-toxic and environmentally-benign, medium for chemical and biological use. In order to make the best use of some of the properties of water as a solvent, it is important that the transition metal complexes exhibit high solubility and good kinetic stability (in some instances) in water. Traditionally, phosphines functionalized with charged/polar substituants (e.g. $-SO_3H$, -COOH or -OH) have been used as ligands to produce aqueous-soluble transition metal complexes. Recently, studies in our laboratories have demonstrated that a new generation of hydroxymethyl-functionalized bis, tris and tetradentate phosphines, upon complexation with the early and late transition metals, produce transition metal complexes possessing water-soluble characteristics. In this presentation, the design and development of water-soluble hydroxymethyl-functionalized phosphines and their application in the development of aqueous-organometallic chemistry will be discussed.

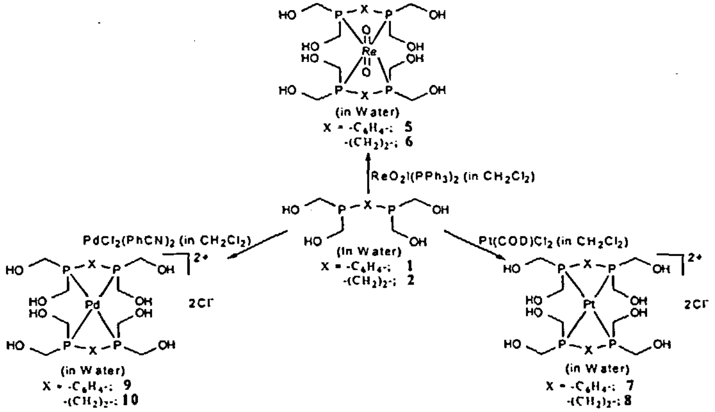
Keywords: Hydroxymethyl Phosphines; Transition Metal Complexes; Tripodal; Biphasic

INTRODUCTION

Chemists have long been interested in the development of chemistry in aqueous-media because water is an environmentally benign solvent. In recent years, chemistry of water-soluble transition metal compounds has gained considerable prominence because of their application in biphasic (aqueous-organic) catalysis and biomedicine. While aqueous-soluble di- or tri- sulphonated aryl phosphines, such as $P(mC_6H_4SO_3Na)_3$, have been, generally, employed in the development of highly active water-soluble transition metal catalysts, hydrophilic alkyl phosphines are being highly sought after in order to gain specific structure-activity advantages. In this contest, our laboratory has developed a series of functionalized water-soluble phosphines that contain hydrophilic hydroxymethyl substituents on the P^{III} center (Figure 1)[1,2]. The coordination chemistry of this class of ligands is discussed herein.

RESULTS AND DISCUSSION

The hydroxymethyl phosphines, summarized in Figure 1, are excellent chelating agents for reactions with early and late transition metals. The reactions outlined in Scheme 1 generally, produced products in excess of 90% yields and occur under aqueous-organic biphasic media [3-5]. For example, the bisphosphines **1** and **2**, dissolved in water, react with $Pt(COD)Cl_2$ (COD = cylooctadine); dissolved in CH_2Cl_2, under biphasic conditions to produce the corresponding water-soluble Pt(II) complexes in near quantitative yields (Scheme 1) [3-5].



Scheme 1

The reactions outlined in Scheme 1 to produce complexes **5-10** are "strictly" biphasic because upon simple vortexing of solution of ligands (in aqueous phase) and metal precursors (dissolved in organic solvents), more than 95% of the metal precursors are transferred into the aqueous media. The metal complexes are isolated in the aqueous phase upon simple separation from the organic phase.

The reactions of **1** (and **2**) with gold(I) precursors, as outlined in Scheme 2, exemplify the rich transition metal chemistry of these ligands to producing products under biphasic conditions. [6-7]

While the reactions summarized in Schemes 1 and 2 provide examples of transition metal complexes (e.g., **5-12**) that possess a ratio of 1:2 between the metal and the coordinated ligand. For specific catalytic applications, it is important to have a ratio of 1:1 between a transition metal and a ligand. In this context, the tripodal phosphine and the thioether functionalized bisphosphines (outlined in Figure 1) provide ample opportunities for tuning the geometries and coordination number of transition metal centers. Figure 2 summarizes the molecular constitutions of Rh(I), Pd(II) and Pt(II) complexes derived from tripodal and tetradentate (P_2S_2) phosphines respectively [8,9].

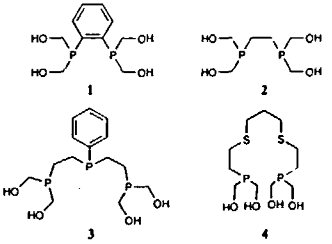
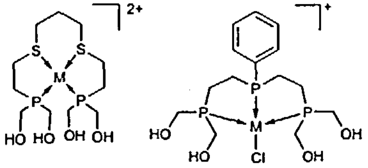


Figure 1

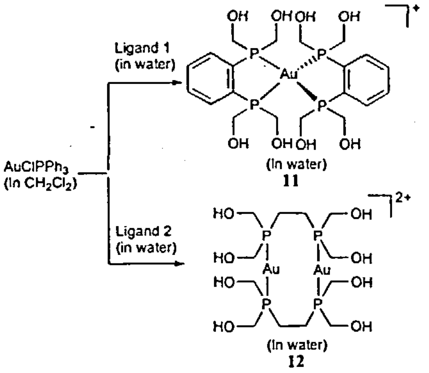


M = Pt: **15**
= Pd: **16**

M = Pt: **13**
Pd: **14**

Figure 2

In biphasic catalysis, the reactants and products stay in the organic phase while the catalyst remains in the aqueous phase. The preferential solubility of HMP complexes (Scheme 1) in aqueous media and their selective partitioning from the organic into aqueous media present prospects for their utility in biphasic catalysis. The chemical modification of the traditional sulphonated-arylphosphines are difficult, making it impractical to tune the lipophilicities of these ligands. Systematic variations in the lipophilicities of ligands and their metal complexes are important in the development of 'counterphase transfer catalysts' wherein a catalyst from the aqueous phase will interact with the lipophilic substrate molecules from the organic phase. As the number of carbon centers in the chemical frameworks of the water-soluble phosphines increases the lipophilic property of the individual ligands also increase accordingly. Therefore, our new approach to ligand design affords phosphines of appropriate aqueous solubility and lipiphilicity (e. g. Compounds **1-4**) for use in the development of counterphase transition metal catalysts for use under aqueous-organic media.



Scheme 2

CONCLUSIONS

Amide, thioether and alkyl functionalized phosphorus(III) hydrides provide examples of skeletal flexibility and can be used as synthons for the development of a new spectrum of water-soluble phosphines. Formylation reactions of functionalized P^{III} hydrides occur under mild conditions to produce hydroxymethyl functionalized water-soluble phosphines. The coordination chemistry of functionalized hydroxymethyl phosphines with early and late transition metals has demonstrated their ability to stabilize specific oxidation states in aqueous media. The high partitioning of these transition metal compounds in water provides new opportunities for the development of water-soluble catalysts for use under aqueous-organic biphasic media.

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