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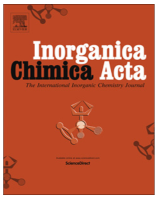

Homogenous catalytic hydrogenation of bicarbonate with water soluble aryl phosphine ligands

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ABSTRACT

The chemical transformation of CO_2 and bicarbonates into useful products becomes increasingly important as the atmospheric CO_2 level has reached 400 ppm. Here a small library of sulfonated aryl monophosphines and aryl diphosphines was tested as stabilizing ligands for a ruthenium catalytic precursor in aqueous-phase bicarbonate hydrogenation to formate. The reactions were monitored by high pressure NMR (HPNMR) spectroscopy which also revealed the presence of stable hydride species possibly linked to the superior activity of certain ligands. The different behaviors observed could be related to variations in air stabilities of the ligands. In some cases a pre-activation step of the catalytic precursor was necessary. The effect of such parameters on the stability and recyclability of the catalytic systems is discussed.

1. Introduction

Carbon dioxide gas (CO_2) is a natural constituent of the atmosphere and an indispensable element of a very complex and delicate balance preserving life. Despite its vital role in biological processes, CO_2 has been recognized as a greenhouse gas with implications in global climate change. The increasing concentration of anthropogenic CO_2 in the atmosphere has urged the scientific community to find ways to activate this thermodynamically and kinetically stable molecule as a feedstock for the production of chemicals and fuels. Therefore, recent scientific developments suggest an alternative perception of CO_2 as a virtually limitless and widely available source of carbon, rather than a "climate killer" [1–5].

Currently CO_2 is serving as a raw material for the industrial production of several compounds, such as urea, salicylic acid, and cyclic carbonates [6]. Thermal, electrochemical and photocatalytic methods for the utilization of CO_2 are also under intense investigation as promising pathways towards numerous products [7,8]. Among them, formic acid (FA), the first reduction product of CO_2 with molecular hydrogen, has recently attracted considerable attention because of its wide area of applications, from leather processing to food preservation, as well as its use as a hydrogen storage material. Catalytic hydrogenation of CO_2 offers an alternative route to the current commercial production of formic acid which utilizes the toxic carbon monoxide or synthesis gas, as well as the possibility of a one-step control of the reaction [9]. Moreover, hydrogenation of bicarbonates and CO_2 to formates and formic acid can be seen as a useful route to hydrogen storage. Hydrogen can then be produced by FA dehydrogenation in a controlled way, allowing for a CO_2-neutral hydrogen storage and release cycle [10].

The hydrogenation of CO_2 to FA in the gas phase being an endergonic reaction ($\Delta G^\circ_{298} = +33\ \mathrm{kJ\ mol^{-1}}$), dissolution of the reactants in water offers a way to overcome this barrier ($\Delta G^\circ_{298} = -4\ \mathrm{kJ\ mol^{-1}}$), while addition of a base further promotes FA formation. During the last decades significant improvements in terms of catalytic activity and productivity have been accomplished in the field of homogenous hydrogenation of CO_2 to FA, as summarized in several reviews and publications [11–14]. When

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the reaction is taking place under acidic conditions, CO_2 is hydrogenated directly to FA, while in an alkaline environment formate is the main product. Most importantly, HCO_3^- and CO_3^{2-} have already been reported to be reduced under mild experimental conditions even in aqueous solutions [15–18]. Utilization of a “green” solvent such as water is highly desirable since it is renewable, non-toxic, non-flammable, relatively inexpensive and the production of waste material (volatile organic solvents and additives) can be minimized.

In order to obtain water soluble catalysts, ligands with hydrophilic substituents are most commonly utilized. Therefore, in this study a series of hydrophilic phosphine ligands bearing biaryl groups and aryl bis(phosphines) containing anionic sulfonate substituents were prepared and tested in the bicarbonate hydrogenation reaction in water without any basic additives. These ligands have recently been reported to be active in the FA dehydrogenation reaction, an important feature for the realization of a carbon neutral hydrogen storage and delivery system [19]. All the ligands were used in combination with the ruthenium precursor $RuCl_3\cdot3H_2O$, and the catalysis followed by applying high pressure NMR techniques. The variations observed in catalytic activities could be caused by steric and/or electronic effects, as well as differences in solubility.

2. Experimental

2.1. Materials and methods

The sulfonated biaryl monophosphine [20,21] and aryl diphosphine [22–24] ligands were synthesized according to literature procedures. All other chemicals are commercial products and were used as received. $RuCl_3\cdot3H_2O$ (99%) was obtained from Precious Metals Online, $NaH^{13}CO_3$, (99% in ^{13}C) from Cambridge Isotope Laboratories and H_2 (99.95%) was supplied by Carbagas-CH. ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Avance DRX 400 MHz (10 mm) spectrometer and the spectra processed with TopSpin and MestReNova. Hydride-containing species were characterized by ^1H NMR spectroscopy using a water suppression pulse sequence tuned to enhance the resolution of the resulting spectrum in the upfield region [25].

2.2. Properties and structures of sulfonated ligands

(See Table 1 and Fig. 1).

2.3. Homogenous catalytic hydrogenation reactions

All catalytic experiments were performed in 10 mm high pressure sapphire NMR tubes [27]. The catalytic species were formed *in situ* by mixing the commercially available $RuCl_3\cdot3H_2O$ (0.028 mmol, 7.3 mg) with either 1.1 (**L6**–**L7**, Fig. 1) or 2.2 (**L1**–**L5**) equivalents of the appropriate phosphine ligand. In a typical experiment the Ru precursor and the ligand were dissolved in 1.5 mL degassed H_2O inside an NMR tube under a N_2 atmosphere and subsequently an aqueous solution of $NaH^{13}CO_3$ (0.1 M) was added. The tube was then pressurized with 80 bar H_2. The reaction was initiated by placing the sapphire tube in the NMR spectrometer already preheated to the desired temperature and monitored by recording ^{13}C NMR spectra at regular intervals of time. Along with the resonance of $NaH^{13}CO_3$ at 160 ppm, a doublet corresponding to $[HCOO]^-$ appears ($\delta = 170$ ppm, $^1J_{C-H} = 195$ Hz). For the recycling experiments the sapphire tube was cooled to room temperature and depressurized, followed by addition of an identical amount of $NaH^{13}CO_3$ as during the first cycle and repressurization with 80 bar H_2. Due to instrumental limitations, during recycling experiments contact with air could not be completely avoided. In order to evaluate the tolerance of the catalytic reaction towards oxygen, a number of experiments without protection against air were also carried out.

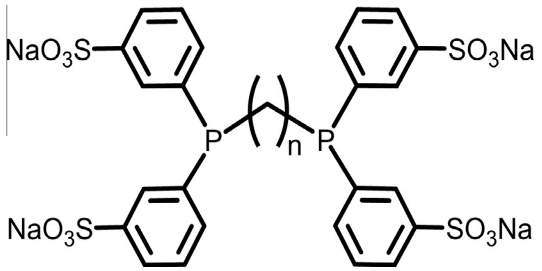
3. Results and discussion

3.1. General considerations

The presence and nature of ligands in homogenous catalysis can significantly alter the behavior of a catalyst. Ligands should offer the appropriate steric and electronic properties to endow the catalyst with optimum activity, selectivity and stability [28]. In order to develop more efficient catalysts, an empirical correlation between their activity and their parameters is desirable. Leitner et al. studied a series of mono- and bidentate phosphine ligands with a rhodium catalytic precursor in $DMSO/NEt_3$ for their activity in the CO_2 hydrogenation reaction [29]. They reported that monodentate phosphines such as PR_3 should possess medium basicity and cone angles <180° in order to form active catalysts. They also found that chelating ligands $R_2P(CH_2)_nPR_2$ ($R =$ alkyl, aryl group) should be of medium ring size ($n = 3, 4$) and that an excess of phosphine ligand is a prerequisite for the reusability of the catalyst.

Jessop et al. [30] examined the correlations between the properties of a series of phosphine ligands and the catalytic activity of ruthenium catalysts in $MeOH/N^iPr_3$ in the hydrogenation reaction of CO_2 to FA. However the results were not conclusive; in the case of monodentate phosphine ligands, electronic factors (i.e., basicity and Hammett constant) were not affecting the activity. On the other hand, weakly basic diphosphines resulted in highly active systems only if their bite angles were small, while more basic diphosphines had the opposite trend. In this case a combination of various properties seemed to be responsible for the observed activity of the resulting catalytic systems rather than a single parameter.

In the present study we examined the effect of different phosphine ligands on the bicarbonate hydrogenation reaction without any organic solvents or amine additives. It has been shown that in water soluble phosphines the removal of a sulfonato group from



n = 2, DPPETS (**L6**)
n = 4, DPPBTS (**L7**)

Fig. 1. Structure of the sulfonated aryl diphosphines.