

# Indium-Based Liquid Clathrates. III. Inclusion Compounds Derived from $[\text{Bu}_4\text{N}][\text{InCl}_3\text{X}]$ Salts and Their Suitability as a Catalysis Medium

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(Received: 10 May 1987; In final form: 11 December 1987)

**Abstract.** Tetrabutylammonium salts of the mixed haloindates,  $[\text{Bu}_4\text{N}][\text{InCl}_3\text{X}]$ ,  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ , interact with aromatic solvents forming liquid inclusion compounds. The aromatic/cation ratio (A/C), a measure of the amount of guest aromatic, has been determined for a variety of simple aromatics. The values range from 2.6 to 0.4, substantially lower than the A/A of similar  $[\text{Bu}_4\text{N}][\text{Al}_2\text{R}_6\text{X}]$  liquid clathrates. The ability of these liquid clathrates to function as catalysis media has been explored. The solubility of  $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl}$  and  $(\text{Ph}_3\text{P})_3\text{RhCl}$  in the various clathrates was determined. It was found that significant leaching of the catalyst into the bulk aromatic solvent occurred, ranging from 13 to 94%. A related liquid clathrate,  $[\text{Li}\cdot 12\text{-crown-4}][\text{InCl}_4\cdot (\text{C}_6\text{H}_5\text{CH}_2)_2]$ , had < 1% of the dissolved catalyst leached.

**Key words.** Liquid clathrate, indium, catalysis.

## 1. Introduction

Liquid clathrate is the term that has been used to describe inclusion complexes formed by interacting aromatic molecules with organoaluminum compounds of the type  $\text{M}[\text{Al}_2\text{R}_6\text{X}]$ . A great many of these have now been described. The subject of liquid clathrates has recently been reviewed [1]. Our previous interests in this area have been concerned with the preparation and structural characterization of the host salts. Unfortunately, solid state X-ray data provides little insight into the nature of guest-host relationships in the inclusion complex. Pulse FT-NMR techniques are quite valuable in this regard, however. This study has been briefly communicated [2]. A full account will be published elsewhere.

Because the guest aromatic is in a unique electronic and geometric environment, we reasoned that interesting arene conversion reactions might be possible. Before such chemistry could be studied, liquid clathrate systems compatible with homogeneous catalysts had to be found. It is the preparation of such inclusion complexes and the determination of their suitability as a catalysis medium that we describe in this report.

## 2. Experimental

All reactions involving aluminum-based liquid clathrates were performed under an inert atmosphere using standard Schlenk techniques. Aromatic solvents were dried over  $\text{LiAlH}_4$  and freshly distilled before use. NMR spectra were recorded on a Perkin Elmer R24-A or JEOL FX200 NMR spectrometer. UV/visible spectra were recorded on a Hewlett Packard 8450 spectrophotometer. The aluminum-based liquid clathrates were prepared according

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to literature procedures [3]. The preparation of [Li·12-crown-4][InCl<sub>4</sub>](C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>)<sub>2</sub> was as described [4]. The [Bu<sub>4</sub>N][InCl<sub>3</sub>X] salts were prepared according to literature procedures [5]. (PPh<sub>3</sub>)<sub>2</sub>Rh(CO)Cl and (PPh<sub>3</sub>)<sub>3</sub>RhCl were commercially obtained and used without further purification.

### 2.1. PREPARATION OF [Bu<sub>4</sub>N][InCl<sub>3</sub>X] LIQUID CLATHRATES

0.005 moles of the appropriate parent salt, [Bu<sub>4</sub>N][InCl<sub>3</sub>X], was dissolved in ~ 10 mL of the aromatic solvent. The aromatic/cation ratios were calculated from the integration of the proton spectra. The alpha protons of tetrabutylammonium ion were used as reference for the integration.

### 2.2. PARTITIONING OF (Ph<sub>3</sub>P)<sub>2</sub>Rh(CO)Cl AND (PPh<sub>3</sub>)<sub>3</sub>RhCl IN [Bu<sub>4</sub>N][InCl<sub>3</sub>X]·(AROMATIC)<sub>x</sub>

Two mL of each inclusion complex was transferred to a flask and the solution saturated with the Rh complex. An equal volume of aromatic was then added and the solution swirled to promote partitioning of the complex between the two phases. A 1 mL aliquot of the excess solvent was removed after settling and diluted ten-fold with additional solvent. The UV/visible spectrum was recorded at 367 nm ((Ph<sub>3</sub>P)<sub>2</sub>Rh(CO)Cl) or 285 nm ((PPh<sub>3</sub>)<sub>3</sub>RhCl) and the concentration of the leached catalyst determined with the aid of a Beer's Law plot prepared from standard solutions of the appropriate Rh complex.

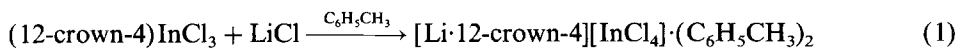
### 2.3. ATTEMPTED HYDROGENATION OF 1-HEPTENE BY (Ph<sub>3</sub>P)<sub>3</sub>RhCl IN [Li·12-CROWN-4][InCl<sub>4</sub>](C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>)<sub>2</sub>

(Ph<sub>3</sub>P)<sub>3</sub>RhCl (3.51 mg, 0.0038 mmol) was added to [Li·12-crown-4][InCl<sub>4</sub>](C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>)<sub>2</sub> (2.2 mL) and stirred until dissolved. The solution was transferred to a test tube fitted with a gas inlet adapter. Toluene (8 mL) was added followed by 1-heptene (0.5 mL). The mixture was stirred and then allowed to stand. The volume of the clathrate layer was observed to decrease by 0.1 mL. The reaction mixture was then warmed and maintained at 55°C in an oil bath. No clouding or discoloration of the clathrate occurred upon warming. Hydrogen was then bubbled through the solution at 10 mL/min. The excess toluene layer was sampled periodically and the composition determined by gas chromatography for a period of 5 hours.

## 3. Results and Discussion

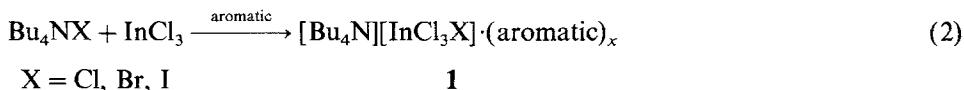
The classical host precursor for liquid clathrates is the anionic organoaluminum adduct, [Al<sub>2</sub>R<sub>6</sub>X]<sup>-</sup>. While these are easy to form, they render the resultant inclusion complex highly air sensitive and chemically reactive. These traits have discouraged the search for applications of these materials. We recently reported the first indium-based liquid clathrate [6]. It was, however, derived from organoindium anions, [In(Cl)I<sub>2</sub>Me]<sup>-</sup> and [In(CH<sub>3</sub>)<sub>2</sub>ICl]<sup>-</sup>, and, consequently, pyrophoric.

While studying crown ether adducts of InCl<sub>3</sub>, we discovered that (12-crown-4)InCl<sub>3</sub> reacts with LiCl in toluene to afford the inorganic-based inclusion complex, equation 1.



The stability of this material prompted us to search for similar indium-derived liquid clathrates.

The tetraalkylammonium tetrahaloindates,  $[\text{R}_4\text{N}][\text{InX}_4]$ , have been known for many years. Their preparation has been performed in either aqueous [7] or alcoholic solution [5] or from melts [8]. We have found that if the reaction is carried out in an aromatic solvent, an inclusion complex results, equation 2.



The value of  $x$  in a classical liquid clathrate represents the number of moles of guest aromatic per mole of anion  $[\text{Al}_2\text{R}_6\text{X}]^-$  (A/A ratio). The parameter is generally determined by  $^1\text{H}$  NMR integration. In **1** the anion is devoid of protons, but a similar technique using the  $[\text{Bu}_4\text{N}]^+$  cation gives a value for  $x$ , which is now more correctly described as the aromatic : cation ratio (A/C). Table I lists the A/C values for a variety of In-based clathrates in different aromatics. As with the aluminum systems, the largest number of guest aromatic generally occurs with the small, symmetrical benzene. The A/C ratios using ethylbenzene, *o*-, *m*-, and *p*-xylene were determined at 80°C in order to suppress the crystallization of the parent salt. Precipitation of the precursor salt is a common occurrence in liquid clathrates, especially for systems which have small amounts of guest aromatic. The other striking feature from Table I is the overall low amount of aromatic that is incorporated relative to an Al liquid clathrate, e.g.  $[\text{Bu}_4\text{N}][\text{Al}_2\text{Me}_6\text{I}]$ , 9.4 vs.  $[\text{Bu}_4\text{N}][\text{InCl}_4]$ , 1.8.

A persistent question about these materials concerns the fundamental nature of a liquid clathrate. The historical answer is that the parent salt forms some type of ordered structure in which aromatic molecules are entrapped [1]. The role of the guest aromatic is to reduce cation-cation repulsion. The role of the anion has largely been ignored. It appears from the data in Tables I and II that the anion merits closer attention.

These tetrahaloindate clathrates are air-stable and offer the potential to provide a unique environment in which to conduct catalytic reactions. To begin studying this possibility, we chose to examine the solubility and stability of two common homogeneous hydrogenation catalysts,  $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl}$  and  $(\text{Ph}_3\text{P})_3\text{RhCl}$ .

Table II lists maximum catalyst concentrations that can be obtained at room temperature. Table II also presents a potential problem with these systems. Since a liquid clathrate is normally prepared with an excess of aromatic present, one must be concerned about leaching of the catalyst from the clathrate into the bulk aromatic phase. As shown in Table II, substantial amounts of catalyst, ranging from 13% to 94%, are partitioned into the bulk aromatic phase when  $[\text{Bu}_4\text{N}]^+$  clathrates are used, making them unacceptable candidates as catalysis media. One clathrate,  $[\text{Li}\cdot 12\text{-crown-4}][\text{InCl}_4] \cdot (\text{C}_6\text{H}_5\text{CH}_3)_2$ , retained essentially all of the dissolved catalyst.

Table I. A/C ratios for the series  $[\text{Bu}_4\text{N}][\text{InCl}_3\text{X}] \cdot (\text{aromatic})_x$  and  $[\text{Li}\cdot 12\text{-crown-4}][\text{InCl}_4] \cdot (\text{aromatic})_x$  in some simple aromatics.

aromatic	$[\text{Bu}_4\text{N}][\text{InCl}_4]$	$[\text{Bu}_4\text{N}][\text{InCl}_3\text{Br}]$	$[\text{Bu}_4\text{N}][\text{InCl}_3\text{I}]$	$[\text{Li}\cdot 12\text{-crown-4}][\text{InCl}_4]$
benzene	1.8(4)	1.4(3)	1.7(3)	2.6(3)
toluene	1.0(2)	1.2(3)	2.1(1)	1.0(1)
ethylbenzene	0.5(2)	1.2(2)	1.0(2)	1.6(2)
<i>o</i> -xylene	1.0(3)	1.4(3)	1.1(2)	1.4(3)
<i>m</i> -xylene	0.6(3)	1.2(4)	1.4(4)	1.1(2)
<i>p</i> -xylene	0.4(2)	0.7(3)	0.5(3)	1.3(2)

Table II. Solubility and leaching of  $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl}$  and  $(\text{Ph}_3\text{P})_3\text{RhCl}$  in  $[\text{Bu}_4\text{N}][\text{InCl}_3\text{X}] \cdot (\text{aromatic})_x$  liquid clathrates.

Clathrate	$(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl}$		$(\text{Ph}_3\text{P})_3\text{RhCl}$	
	maximum conc. at 25°C $\times 10^{-3}$ M	% leached by excess aromatic	maximum conc. at 25°C $\times 10^{-3}$ M	% leached by excess aromatic
$[\text{Bu}_4\text{N}][\text{InCl}_4] \cdot (\text{C}_6\text{H}_6)_{1.8}$	7.7	47	5.8	13
$[\text{Bu}_4\text{N}][\text{InCl}_3\text{Br}] \cdot (\text{C}_6\text{H}_6)_{1.4}$	4.0	72	3.3	94
$[\text{Bu}_4\text{N}][\text{InCl}_3\text{I}] \cdot (\text{C}_6\text{H}_5\text{CH}_3)_{2.1}$	7.1	27	6.6	19
$[\text{Li} \cdot 12\text{-crown-4}][\text{InCl}_4] \cdot (\text{C}_6\text{H}_5\text{CH}_3)_2$	7.1	15	1.7	<1

The  $(\text{Ph}_3\text{P})_3\text{RhCl}$  catalyzed hydrogenation of heptene to heptane was attempted using this system. No reaction occurred. In retrospect, this may not be too surprising since  $(\text{Ph}_3\text{P})_3\text{RhCl}$  is inactive in halogenated solvents [9]. Perhaps the tetrachloroindate is causing a similar inhibitory effect, making Rh-catalyzed olefin hydrogenation a less than fortuitous choice as an initial screening reaction.

### Acknowledgement

We acknowledge the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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