Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 690 (2005) 3552–3557

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Searching for molecular arene hydrogenation catalysis in ionic liquids

Tilmann J. Geldbach, Paul J. Dyson *

Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Received 9 February 2005; received in revised form 3 March 2005; accepted 3 March 2005
Available online 13 April 2005

Abstract

Arene hydrogenation by homogeneous catalysts is a highly controversial area of research, with many of the mononuclear complexes shown to catalyse the reaction, being found to be pre-catalysts to nanoparticles, on closer examination. The solvent properties of ionic liquids, i.e., low nucleophilicity and high polarity, make them ideal, at least in principal, for homogeneous arene hydrogenation catalysts. In this paper, we described our attempts to prepare and study such systems, using either simple metal halides or ruthenium complexes including trinuclear ruthenium clusters as catalyst precursors.

Keywords: Hydrogenation; Biphasic catalysis; Cluster; Ionic liquid; Ruthenium

1. Introduction

The hydrogenation of benzene and other arenes by molecular catalysts is a fascinating and controversial area of research, in which many highly innovative catalysts have been evaluated. Arene hydrogenation is not just a topic of academic interest, but has industrial application such as the synthesis of cyclohexane (a precursor to adiptic acid used to produce nylon) [1], removal of aromatic compounds from fuels [2], and as way to prevent paper from yellowing without addition of bleaches, since the compounds responsible for the yellowing are aromatic macromolecules [3]. All industrial arene hydrogenation catalysts are heterogeneous, including a system that converts benzene to cyclohexene, which is subsequently converted into cyclohexanol [4]. However, there is some interest in finding versatile and selective homogeneous catalysts for the synthesis of fine chemicals, because many substituted arenes are readily available and the most convenient route to a cyclohexyl-analogue would be via hydrogenation at one side of the arene ring [5].

A large number of molecular compounds have been used as pre-catalysts for the hydrogenation of benzene and arenes [6], and some have since been shown to be precursors to heterogeneous catalysts, such as soluble nanoparticles, with many more cases suspected [7]. Most of the catalyst precursors are based on platinum group metals, although not exclusively, and often contain an arene ligand or labile ligands [6]. A mechanism for arene reduction was thus proposed invoking a stepwise hydrogenation-slippage process in which each unsaturated bond of the arene is hydrogenated in turn (see Scheme 1) [8].

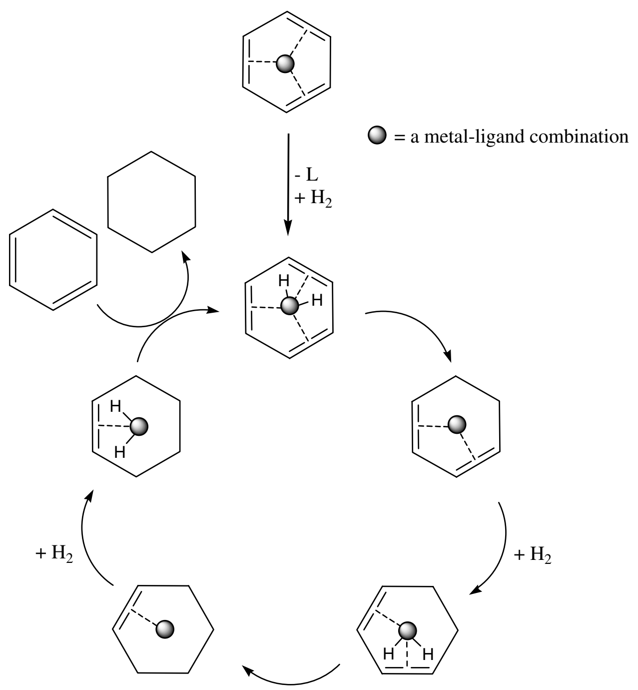
What is interesting to note, and contrasts with the usual perception of homogeneous catalysis, is that soluble colloidal (or nanoparticle) arene hydrogenation catalysis tend to operate under milder conditions and exhibit higher activities than molecular catalysts [9]. One explanation for this dichotomy is that the homogeneous arene hydrogenation catalysts are not homogeneous in the first place, as mentioned above. Another possibility is that the arene, when coordinated to the nanoparticle surface, is more highly activated than when

---

* Corresponding author. Tel.: +41 21 693 98 54; fax: +41 21 693 98 85.

E-mail address: paul.dyson@epfl.ch (P.J. Dyson).

0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.03.006



Scheme 1. The arene-exchange mechanism for the reduction of arenes.

coordinated to a single metal centre. Accordingly, benzene and other arenes have been shown to lie over three metal centres on certain surfaces [10], and such a bonding regime has also been observed in molecular cluster compounds [11]. In this so called μ_3–η^2:η^2:η^2 bonding mode an arene is more highly activated as demonstrated by a Kekulé-like structure combined with indicative spectroscopic data [12]. Thus, clusters where such coordination is possible could prove to be the missing link and might provide definitive proof for homogeneous arene hydrogenation. In addition, since it has recently been shown that catalysis by intact clusters is favoured in polar solvents [13], non-coordinating ionic solvents could facilitate arene hydrogenation [14]. Catalysis by clusters is a well established process [15] and has already been demonstrated in ionic liquids [16]. Nanoparticle catalysis in ionic liquids has also been demonstrated [17] including, remarkably, partial reduction of benzene to cyclohexene [17a].

2. Results and discussion

The acidic chloroaluminate ionic liquid [*N*-ethyl-*N*-methyl-imidazolium]Cl–$AlCl_3$ ($x = 0.67$), combined with electropositive metals such as aluminium, zinc or lithium together with a proton source, have previously been shown to hydrogenate aromatic compounds, and the partial reduction of polyaromatic compounds was also achieved [18]. In addition, the titanium complex Ti(η^6-C_6H_5Me)Al_2Cl_8 is a pre-catalyst for the conversion of benzene to cyclohexane in molecular solvents [19]. Some decomposition of the titanium complex was observed during the reaction and the possibility that metallic particles were responsible for the catalysis cannot be discounted.

Simple metal halides can form arene–metal complexes under reducing conditions [20]. Thus, attempts to generate catalysts from metal chlorides in the Lewis acidic chloroaluminate ionic liquid [*N*-octyl-3-picolinium]Cl–$AlCl_3$, were undertaken in the first instance. Essentially, the metal chloride was dissolved in the ionic liquid and benzene added, affording a biphasic mixture. The system was then pressurized with H_2 to 50 bar, stirred at 100 °C for 4 h and the conversion determined by GC. The results from these experiments are summarized in Table 1. A first approximation of the course of the reaction is possible by looking at the two different phases. While cyclohexane is immiscible with the ionic liquid, affording a colourless upper phase, benzene is partially miscible with the chloroaluminate ionic liquid as is visible from a markedly coloured organic phase.

Of the seven salts screened only $PdCl_2$ and K_2PtCl_4 showed significant activities, the platinum salt giving almost quantitative conversion to cyclohexane under the conditions employed, with no indication of the formation of either cyclohexene or cyclohexadienes. For this reason, and because under reducing conditions platinum salts are known to form cluster compounds [21], K_2PtCl_4 was investigated further. Under essentially the same conditions, except with a shorter reaction time to ensure the reaction did not go to completion, the effect of catalyst concentration was studied and the results are listed in Table 2. In all the reactions, with the exception of those employing 1 and 3 mg of K_2PtCl_4, deposits of platinum black were present. This observation indicates that the active catalyst could in fact be heterogeneous and not homogeneous. Recycling of the system was attempted and in general slightly lower conversions were observed compared to those obtained in the first cycle.

Next, the effect of temperature was explored and while a reduction in the reaction temperature to 20 °C

Table 1
Conversion of benzene to cyclohexane using metal chlorides dissolved in [*N*-octyl-3-picolinium]Cl–$AlCl_3$[a]

Metal chloride	Benzene (%)	Cyclohexane (%)
$ZrCl_4$	100	–
$NiCl_2$	100	–
$PdCl_2$	43	57
$CrCl_3$	99.5	0.5
K_2PtCl_4	1	99
$CoCl_2$	100	–
$SmCl_3$	100	–

[a] [*N*-octyl-3-picolinium]Cl–$AlCl_3$ (1.5 ml), benzene (3 ml), H_2 (50 bar), $t = 240$ min, $T = 100$ °C. Conversion determined by GC.