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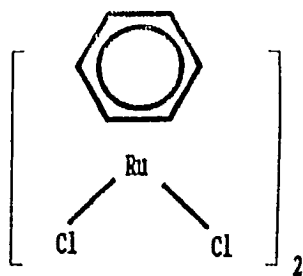
The impetus for the use of homogeneous catalysts for effecting hydrogenation and organic reactions has come from the recognition that these compounds possess the advantage of high selectivity and yield under mild conditions [1-3]. A significant breakthrough in the field of homogeneous hydrogenation catalysis was the synthesis of an active rhodium (I) complex, $\text{HRhCl}(\text{PPh}_3)_3$, and the ruthenium complex, $\text{HRuCl}(\text{PPh}_3)_3$, by Wilkinson and coworkers [4,5]. A number of similar transition metal complexes have been synthesized and studied for catalytic hydrogenation [1-3,6].

In the oil and gas industry, the use of heterogeneous catalysts is far more common because it is easier to separate the solid catalyst from products and reactants. Separation may become tedious and difficult in homogeneous systems, such as distillation in Wacker process, or the addition of immiscible solvents in the Shell Higher Olefins Process. In order to economize and simplify the catalyst recovery in biphasic systems, water, which is immiscible with most organic products, is an obvious choice of solvent. However, hydrogenation catalysis in biphasic conditions may require the development of water soluble organometallic catalysts and new separation processes, such as membrane separations.

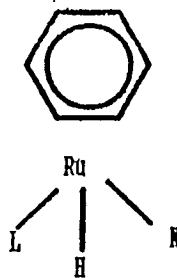
Catalysts containing water soluble phosphine ligands such as $\text{P}(\text{C}_6\text{H}_4\text{SO}_3\text{Na})_3$ have been used under two-phase aqueous-organic conditions [7]. However, phase transfer conditions such as the addition of quaternary ammonium salts or other phase transfer agents are often required for these reactions to be effective. Nonetheless, hydroformylation of lipophilic propylene in water with $\text{HRhCO}(\text{P}(\text{C}_6\text{H}_4\text{SO}_3\text{Na})_3)_2$ complex may constitute the first and possibly the best example of biphasic organometallic catalysis [8]. Recently, asymmetric hydrogenation in a two phase aqueous-organic medium was reported using a rhodium complex associated with chiral sulphonated phosphines [9].

Although numerous ruthenium and rhodium complexes have been investigated [6,7,9-11], there have been no reports, to our knowledge, on the use of Bis dichloro (η^6 -benzene) $\text{Ru}(\text{II})$ dimer (Ru_2Cl_2) (I) for hydrogenating an aromatic ring under biphasic aqueous-organic conditions. We report in this communication the first example of the use of this organometallic complex in the reduction of aromatic rings in a biphasic aqueous-organic system.

This ruthenium dimer (I) has been reported as a homogeneous catalyst for the hydrogenation and isomerization of olefins, namely, 1-pentene, 2-pentene, 1-hexene and cyclooctene in the presence of a base such as triethylamine and pyrrolidine in polar coordinating solvents [12,13]. Recently, we have also observed that cyclic-olefins and quinolines can be hydrogenated to corresponding cycloalkanes and tetrahydroquinolines by this ruthenium dimer (I), in the presence of a base under mild conditions [14]. It was envisioned that selectivity in the hydrogenation reaction could be induced by an appropriate choice of the solvent system and substrate. Organoruthenium complex (I) is soluble in water. Moreover, benzene is approximately 3.5 times more soluble in aqueous phase than toluene, which is 2.5 times more than xylenes. As a rational approach towards exploitation of this selectivity in solubility, we studied the hydrogenation of model substrates in a biphasic aqueous-organic system utilizing ruthenium dimer (I) as catalyst precursor. Indeed, our results demonstrated the selectivity in hydrogenation of the benzene ring over other aromatics, Table 1. It is highly probable that the reaction involves the interaction between benzene dissolved in the bulk aqueous phase and piano stool organoruthenium hydride complex, (II). A noteworthy feature of the system is that a phase transfer agent is not required.



I



II

L, M = ligands

In a typical experiment, a predetermined amount of ruthenium dimer (I) and substrate (Table 1) was placed in a glass-lined stainless steel autoclave which was purged three times with hydrogen and then charged to desired pressure and temperature. The hydrogenation reaction was carried out at 70°C and 460 psig for 24h with constant stirring. Hydrogenation was confirmed by quantitative analysis of the organic phase on capillary GC. Only cyclohexane and methylcyclohexane were produced from benzene and toluene hydrogenation in these experiments.

TABLE 1

Experimental hydrogenation results

| Reactants | | | | | Conversions | | |
|----------------|----------------|----------------|--------------|------------------|----------------|----------------|----------------|
| Benzene (g) | Toluene (g) | Xylenes (g) | Water (g) | Catalyst (mg) | Benzene (%) | Toluene (%) | Xylenes (%) |
| 5.205 | 16.218 | 0.199 | 2.075 | 25 | 47.9 | 16.8 | none |
| 3.477 | 18.418 | 0.256 | 3.768 | 30 | 37.5 | 24.0 | none |

In conclusion, we have shown that Bis dichloro (η^6 -benzene) Ru(II) dimer serves as an efficient catalyst precursor for hydrogenation of an aromatic ring under biphasic conditions. Moreover, the activity and selectivity of the reaction may be controlled by reaction conditions, in addition to variation in the structure of the catalyst. An important practical consequence of this biphasic system is the easy separation of hydrocarbon layer from the aqueous portion containing catalyst. It is apparent, therefore, that water soluble organometallic complexes hold significant promise for selective catalytic hydrogenation. Further scope and limitations for the catalytic hydrogenation of the aromatic ring under biphasic conditions using organoruthenium and other transition metal complexes are still under investigation.

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