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A Highly Selective Arene Hydrogenation Catalyst that Operates in Ionic Liquid

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Aromatic compounds are notoriously difficult substrates to hydrogenate, although a wide range of reagents have been used for this purpose.[1] It has been proposed that because chemistry of aromatic compounds is so vast, the most obvious route to stereodefined unsaturated cyclic compounds is to construct the appropriate aromatic compound and then reduce it in a stereoselective fashion. The majority of the reagents used to hydrogenate aromatic compounds are used in stoichiometric quantities, such as the Birch method that employs group 1 or 2 metals dissolved in liquid ammonia.[2] In contrast, effective homogeneous catalysts are relatively rare, although several ingenious systems have been reported. For example, Rothwell has developed a series of homogeneous niobium- and tantalum-based catalysts,[3] Süss-Fink has described a number of robust cluster catalysts that operate under aqueous−organic biphasic conditions,[4] and Angelici has supported some rhodium complexes onto metal-impregnated porous supports that results in highly active catalysts.[5] We have also shown that arenes can be hydrogenated using an ionic liquid-organic biphasic protocol.[6] In this paper, we describe a new arene hydrogenation catalyst that is active in organic solvents, but considerably more active in ionic liquids, and, remarkably, will hydrogenate the arene ring of allylbenzene without hydrogenating the alkene bond.

The reaction of the triply bridged chloro-dimer, [(η^6-*p*-cymene)$_2$-Ru$_2$(μ-Cl)$_3$][PF$_6$], with 2 equiv of 1,1,1-tris(diphenylphosphinomethyl)ethane (TRIPHOS) in the presence of 1 equiv of ammonium hexafluorophosphate in methanol under reflux affords [Ru(η^6-*p*-cymene)(η^2-TRIPHOS)Cl][PF$_6$] **1**·[PF$_6$] in high yield.[7] The ^{1}H NMR spectrum of **1** is quite complicated and shows that the six-membered ring formed by the ruthenium and TRIPHOS ligand exists in chair and boat conformations in a similar way to other compounds previously reported.[8] The structure of **1** has been established by single-crystal X-ray diffraction using a crystal grown from a dichloromethane-methanol solution by slow diffusion.[9] The structure of **1** is shown in the Supporting Information. The geometry around the Ru atom is essentially octahedral, made up by the arene [mean Ru−C 2.28 Å], the chlorine ligand [Ru−Cl 2.3900(10) Å], and two of the three phosphine donors [mean Ru−P 2.338 Å] which form a six-membered ring with a chair conformation. The third phosphine unit resides at quite a distance from the Ru atom. The structure around the ruthenium center is similar to other cationic Ru(arene)(diphosphine)chloride complexes previously described.[10] The bonding mode for the TRIPHOS ligand has also been observed previously, although those in which the free phosphine remains unoxidized are very rare.[11]

The extensive hydrophobic region provided by the TRIPHOS ligand has been proposed to facilitate catalytic processes by promoting the interaction of the coordinated metal center with small organic molecules.[12] Compound **1** has been evaluated in dichloromethane under homogeneous conditions and in 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid, [bmim][BF$_4$], under biphasic conditions and has proven to be a highly active arene hydrogenation catalyst. The results from some of these reactions are summarized in Table 1, and a more extensive list is given in the Supporting Information. Overall, the results show the expected trend for the hydrogenation of arene substrates,[4] in that the highest turnover is observed for the hydrogenation of benzene, with turnovers decreasing as the size or number of alkyl substituents increases on the arene substrate. What is surprising is that **1** is essentially inactive toward arenes with α-alkene substituents such as styrene and 1,3-divinylbenzene, whereas the turnover for the hydrogenation of allylbenzene to allylcyclohexane is considerably higher than expected, ca. 329 mol mol^{-1} h^{-1} as compared to 205 and 127 mol mol^{-1} h^{-1} for toluene and ethylbenzene, respectively. Furthermore, the alkene bond remains unhydrogenated. Hydrogenation of alkene substrates such as 1-hexene and 1-octene was attempted with **1** as the catalyst, which gave very low turnover numbers, in part because of catalyst decomposition, but suggesting that this catalyst has considerable potential in organic synthesis.

Arene hydrogenation using **1** is believed to take place via a slippage mechanism, the preferred mechanism for arene hydrogenation in organic synthesis. Although we do not have direct evidence that such a mechanism is in operation, there is convincing circumstantial evidence. First, the presence of mercury, employed as a selective poison toward colloids, did not effect activity. Second, the catalyst is recovered, albeit with the substrate arene in place of the *p*-cymene in the starting material, intact. Third, hydrogenation of C$_6$D$_6$ affords only a single isomer of C$_6$D$_6$H$_6$, demonstrating that the hydrogen atoms have been introduced to the arene ring from one side only, indicative of the addition occurring to a coordinated arene.[14] It is not immediately obvious why styrene and divinylbenzene are resistant to hydrogenation. It is possible that they form an η^4 interaction via the vinyl double bond and the arene which inhibits hydrogenation. It would appear that the third, free phosphine is essential in providing selectivity toward the hydrogenation of arenes. When this phosphine is blocked by coordination to a nonactive metal, the resulting material does not hydrogenate arenes, but becomes active toward alkene substrates. We propose that the free phosphine assists the hydrogenation of arenes by

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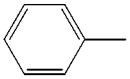
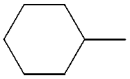
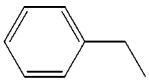
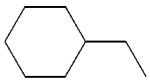
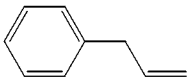
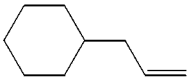
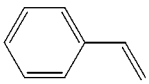
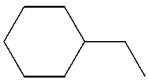
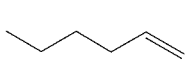
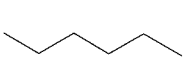
Table 1. Hydrogenation of Some Arenes Using **1**·[PF_6] in [bmim][BF_4][13]

Substrate	Product	Turnover frequency ($molmol^{-1}h^{-1}$)
		476 242 (CH_2Cl_2)
		205 74 (CH_2Cl_2)
		127 57 (CH_2Cl_2)
		329
		3
		16

reversible coordination to the ruthenium involving an "arm-on/off" mechanism proposed previously.[15] This could have the effect of causing the ring to slip from the η^6 to η^4 mode, thereby promoting hydrogenation of the uncoordinated arene C═C double bond. We intend to report more fully on this in the future. A cobalt complex has previously been shown to catalyze the reduction of allylbenzene to allylcyclohexane in 2% yield along with other hydrogenation products,[16] and it has been postulated that such a conversion is not unreasonable when catalyzed by a d^6 metal center,[17] although we are not aware of any other examples.

As mentioned above, **1** was examined in both dichloromethane and ionic liquid solutions for comparison purposes. Although the latter system is biphasic, it is considerably superior, although we have previously shown that ionic liquids are not always superior solvents for conducting hydrogenation reactions.[18] Not only are the turnovers significantly higher, but, over a number of runs, the catalyst decomposes in dichloromethane, whereas in [bmim][BF_4] no depreciation in activity is observed after five runs.

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Supporting Information Available: Tables of hydrogenation data for **1**·[PF_6], crystal data, figure of the molecular structure of the cation and selected bond parameters, structure solution and refinement, atomic coordinates, full bond lengths and bond angles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Synthesis and characterisation of **1**: A solution of [(η^6-*p*-cymene)$_2$$Ru_2$-($\mu$-Cl)$_3$][$PF_6$] (500 mg, 0.693 mmol), 1,1,1-tris(diphenylphosphinomethyl)-ethane, TRIPHOS (866 mg, 1.386 mmol), and NH_4PF_6 (113 mg, 0.693 mmol) in methanol (200 mL) was refluxed for 4 h. After being cooled to room temperature, filtration of the solution, followed by the removal of the solvent under reduced pressure and washing with cold ethanol and diethyl ether, afforded a yellow microcrystalline solid (1424 mg, 1.368 mmol, 98.7% yield/Ru). Single crystals for X-ray structural determination were grown using liquid diffusion of hexane into a dichloromethane solution of **1**. Positive ion electrospray mass spectrum *m*/*z* 895 [Ru(η^6-*p*-cymene)(η^2-TRIPHOS)Cl]$^+$, *m*/*z* 761 [Ru(TRIPHOS)Cl]$^+$; ^{31}P-{^{1}H} NMR ($CDCl_3$) 26.51 (s), 24.72 (s), −28.40 (s), −29.66 (s), −142.95 (septet, J = 708.95 Hz) ppm; ^{1}H NMR* ($CDCl_3$) 7.6−6.8 (m, boat/chair), 5.72−5.46 (m, boat/chair), 3.37 (d, J = 14.5 Hz, boat 1H), 3.13 (dt, J = 15.0 Hz, J = 4.0 Hz, chair 1H), 2.32 (m, chair 1H), 2.25 (s, chair 2H), 2.13 (m, boat 1H), 2.07 (septet, J = 6.86 Hz, boat 1H), 1.75 (s, boat 3H), 1.69 (s, boat 2H), 1.56 (septet, J = 6.86 Hz, chair 1H), 1.20 (s, chair 3H), 1.03 (s, boat 3H), 0.74 (m, boat/chair), 0.14 (s, chair 3H) ppm.
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(9) Crystal data: (120 K) $C_{51}H_{53}ClF_6P_4Ru$, MW = 1040.33, monoclinic $P2_1/n$, a = 12.431(3) Å, b_3 = 21.714(4) Å, c_1 = 17.416(4) Å, β = 98.23(3)°, Z = 4, V = 4652.7(16) Å^3, μ = 0.592 mm^{-1}, 10 461 unique reflections, R1 = 0.0579 (0.0919 for all data), wR2 = 0.1384 (0.1575 for all data). Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-189682 (**1**·PF_6). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail deposit@ccdc.cam.ac.uk).
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