Hydrodechlorination of Chloroaromatics: the Use of a Bifunctional Homogeneous Rhodium Catalyst for the Conversion of Chloroaromatics into Saturated Hydrocarbons

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The catalytic conversion of chloroaromatics into the corresponding saturated hydrocarbons is catalysed by a bifunctional homogeneous rhodium catalyst system generated from $[(C_5Me_5)RhCl_2]_2$ in the presence of an excess of NEt_3 under 600 psi H_2 at 75 °C (1 psi $\approx 6.894757 \times 10^3$ Pa).

The development of new processes for the effective removal of highly toxic chloroaromatics from the environment has received much attention.[1] Most of the technologies used are based on stoichiometric or catalytic dechlorination resulting in aromatic hydrocarbons.[2] It has been shown that catalytic hydrogenolysis could be also used for dechlorination.[3] However, hydrogenolysis of single ring chloroaromatics produces benzene, which is also highly toxic and therefore must be removed. Since the catalytic hydrogenation of aromatics[4] can be performed under similar conditions to those used for hydrogenolysis, the combination of these two reactions could lead to a novel dechlorination process.

We now report that the homogeneous catalytic hydrodechlorination of chloroaromatics to the corresponding aromatic hydrocarbons followed by *in situ* hydrogenation to the saturated hydrocarbons is catalysed by the same rhodium catalyst system generated from $[(C_5Me_5)RhCl_2]_2$ in the presence of NEt_3.[4][†] The process requires an excess of NEt_3 with respect to the total number of chlorine atoms in the chloroaromatics for the removal of the hydrogenolysis product HCl and can be recovered by the treatment of $[HNEt_3]Cl$ with aqueous base. The individual steps of this process for chlorobenzene are shown in eqns. (1)–(4).

$$C_6H_5\text{–}Cl + H_2 \rightarrow C_6H_6 + HCl \quad (1)$$

$$C_6H_6 + 3\,H_2 \rightarrow C_6H_{12} \quad (2)$$

$$HCl + NEt_3 \rightarrow [HNEt_3]Cl \quad (3)$$

$$[HNEt_3]Cl + NaOH \rightarrow NEt_3 + NaCl + H_2O \quad (4)$$

A typical catalyst is prepared by dissolving $[(Me_5C_5)RhCl_2]_2$ in isopropanol in the presence of an excess of NEt_3. The reactions are performed in a stainless steel autoclave under 600 psi H_2 at 75 °C and the results for chlorobenzene, 1,2,4-trichlorobenzene and chloronaphthalene are shown in Tables 1–3. It appears that in all cases the hydrogenolysis of

Table 1 Treatment of chlorobenzene (1 mmol) with H_2 (600 psi) in the presence of NEt_3 (10 mmol) using $[(Me_5C_5)RhCl_2]_2$ (0.03 mmol) in 25 ml Me_2CHOH at 75 °C

	Time/min						
	0	30	60	90	120	180	240
C_6H_5Cl (%)	100	86.4	67.7	46.6	20.2	0	0
C_6H_6 (%)	0	7.2	14.4	19.9	21.6	3	0
C_6H_{12} (%)	0	6.4	17.9	33.6	58.2	97	100

Table 2 Treatment of 1,2,4-trichlorobenzene (1 mmol) with H_2 (600 psi) in the presence of NEt_3 (10 mmol) using $[(Me_5C_5)RhCl_2]_2$ (0.03 mmol) in 25 ml Me_2CHOH at 75 °C

	Time/min					
	0	30	60	120	240	360
$C_6H_3Cl_3$ (%)	100	96	87	69	35	0
$C_6H_4Cl_2$ (%)	0	4	12	21	13	0
C_6H_5Cl (%)	0	0	1	3	4	0
C_6H_6 (%)	0	0	0	2	6	0
C_6H_{12} (%)	0	0	0	4	41	100

Table 3 Treatment of 1-chloronaphthalene (1 mmol) with H_2 (600 psi) in the presence of NEt_3 (10 mmol) using $[(Me_5C_5)RhCl_2]_2$ (0.03 mmol) in 25 ml Me_2CHOH at 75 °C

	Time/min						
	0	30	60	90	120	180	240
$C_{10}H_7Cl$ (%)	100	57.7	7.7	0	0	0	0
$C_{10}H_8$ (%)	0	29.2	20.0	0	0	0	0
$C_{10}H_{12}$ (%)	0	9.4	41.0	35.7	26.2	10.7	2.3
$C_{10}H_{18}$ (%)	0	3.8	31.3	64.3	73.8	89.3	97.7

[†] The hydrogenation of aromatics using $[Me_5C_5RhCl_2]_2$ in the presence of NEt_3 was reported by Maitlis.[4] The base is required to neutralize the HCl that is formed during the activation of H_2 by $[Me_5C_5RhCl_2]_2$.

the C_{arene}–Cl bonds occurs first resulting in the transient formation of the corresponding but lower chlorine containing aromatics and finally a chlorine-free aromatic compound, which is then hydrogenated to the saturated hydrocarbon. This is supported by the fact that cyclohexyl chloride cannot be hydrodechlorinated under the same conditions. It should be noted that when a mixture of cyclohexyl chloride and chloronaphthalene was used as substrate only the latter reacted, as expected.

Some aspects of the mechanism of these reactions were studied by using chlorobenzene as substrate. The hydrogenation of $[^2H_5]$chlorobenzene resulted in $[^2H_5]$benzene which is hydrogenated to $[^2H_5]$cyclohexane.‡ The transient formation of $[^2H_5]$benzene provides further evidence that the hydrodechlorination occurs prior to hydrogenation, and that the intermediate involved in the hydrogenolysis of the C_{arene}–Cl bond does not scramble. Furthermore, the hydrodechlorination step does not involve the addition of H_2 followed by the elimination of HCl. Finally, the rates of the hydrodechlorination of chlorobenzene were practically the same when 1.2 or 9 equiv. of NEt_3 were used. These results suggest that the role of the NEt_3 is to scavenge the HCl eliminated from rhodium species.

In conclusion, we have shown that chloroaromatics could be converted to chlorine-free nonaromatic compounds of much less environmental concern. Furthermore, the successful application of the same catalyst system for two reactions in one pot demonstrates the great opportunities for bifunctional homogeneous transition metal catalysts.

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References

1 O. Hutzinger, S. Safe and V. Zitko, *The Chemistry of PCBs*, CRC Press, Cleveland, OH, 1974.

2 D. G. Ackerman, L. L. Scinto, P. S. Bakshi, R. G. Delumyea, R. J. Johnson, G. Richard, A. M. Takata and E. M. Sworzyn, *Destruction and Disposal of PCBs by Thermal and Non-Thermal Methods*, NDC, Park Ridge, NJ, 1983.

3 V. V. Grushin and H. Alper, *Organometallics*, 1991, **10**, 1620.

4 P. M. Maitlis, *Acc. Chem. Res.*, 1978, **11**, 301; M. A. Bennett, *CHEMTECH* 1980, 444; R. H. Fish, *Aspects Homogeneous Catal.*, 1990, **7**, 65.

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‡ The elucidation of the stereochemistry of $[^2H_5]$cyclohexane is in progress.