Rhodium(III) biphasic and phase-transfer-catalyzed hydrogenolysis of chloroarenes under exceptionally mild conditions

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Fourier maps. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Hydrogen atoms were added at calculated positions and included in the structure factor calculations with a common thermal parameter (U = 0.08 Å^2).

Of 8394 reflections, measured with an 2θ–ω scan technique in the range $3 < 2\theta < 50°$, 4630 having $I > 3\sigma(I)$ were used to refine 518 parameters to final residuals of R = 0.045 and R_w = 0.049.

The weighting scheme used in the last refinement cycles was $w = 1.000/(\sigma^2(F_o)+0.001163F_o^2)$, which showed reasonable consistency in a test of $w\Delta^2$ for data sectioned with respect to both F_o and $(\sin\theta)/\lambda$. Scattering factors for non-hydrogen atoms were taken from ref 28 and for hydrogen atoms from ref 29. Anomalous dispersion corrections for Rh, Pd, Cl, and P atoms were taken from ref 30.

All calculations were performed with SHELX76[31] and PARST[32] sets of programs on the IBM 4341 computer at the "Centro di Calcolo dell' Università di Messina". The refined structure was plotted with use of the ORTEP program (Figure 1). Full lists of bond distances and angles, hydrogen coordinates, anisotropic temperature factors, and calculated and observed structure factors are available as supplementary material. Non-hydrogen coordinates are shown in Table I.

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Supplementary Material Available: Tables listing crystallographic parameters, anisotropic thermal parameters for non-H atoms, fractional atomic coordinates for H atoms, and complete bond lengths and angles (5 pages); a table of structure factors (26 pages). Ordering information is given on any current masthead page.

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Rhodium(III) Biphasic and Phase-Transfer-Catalyzed Hydrogenolysis of Chloroarenes under Exceptionally Mild Conditions

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The rhodium(III) complexes $L_2Rh(H)Cl_2$ [L = tricyclohexylphosphine or triisopropylphosphine] are excellent catalysts for the hydrogenolysis of chloroarenes. The reaction proceeds under biphasic [40% NaOH, $PhCH_3$] conditions, or to give somewhat higher product yields, under phase-transfer conditions, using benzyltriethylammonium chloride as the quaternary ammonium salt. The reaction occurs under mild conditions, and many functional groups [e.g. R, OR, CF_3, COAr, COOH, NH_2] are compatible for the carbon–chlorine bond cleavage process.

Carbon–halogen bonds in aromatic compounds are usually quite resistant to reactions with nucleophiles and transition metal complexes. Aryl iodides, which are expensive, are able to undergo Ullmann[1] and $S_{RN}1$ type[2] transformations. They can also participate in transition-metal-catalyzed cross-coupling reactions, olefin arylation reactions as well as some carbonylation processes.[3] Bromoarenes are appreciably less reactive substrates in all of these reactions. The cheapest haloarenes, chlorobenzenes, are much more inert and are usually incapable of undergoing reactions observed with iodoarenes and bromoarenes. Recently, carbonylation reactions of chloroarenes have been discovered by the use of novel palladium complexes as catalysts.[4] The low chemical reactivity of the aryl carbon–chlorine bond can be rationalized on the basis of kinetic and thermodynamic (D_{Ph-Cl} = 96 kcal/mol)[5] factors.

Phase-transfer catalysis (PTC) has been widely used in the synthesis of organometallic complexes and for transition-metal-catalyzed organic reactions.[6] Recently, PTC was shown to be effective for the generation of electron-rich and coordinatively unsaturated transition-metal complexes by reductive elimination of hydrogen chloride from some hydrido transition-metal chlorides (eq 1).[7] For example,

$$L_nM(H)(Cl) \xrightarrow[PTC]{-HCl} L_nM \tag{1}$$

the rhodium hydrides $[(Cy_3P)_2Rh(H)Cl_2]$ (Cy = cyclohexyl; 1) and $[(i\text{-}Pr_3P)_2Rh(H)Cl_2]$ (i-Pr = isopropyl; 2), in the presence of KOH or NaOH, are able to catalyze H/D exchange between dihydrogen and aromatic hydrocarbons.[8]

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Table I. Hydrogenolysis of Chloroarenes by H_2/1/$PhCH_2N(C_2H_5)_3^+Cl^-$/40% NaOH

chloroarene (amt, mmol)	amt of $PhCH_3$, mL	1, mol %	*T*, °C	time, h	product	yield,[a] %
chlorobenzene (1.4)	1.0	5	25	24	benzene	(97)
1-chloronaphthalene (10)	1.0	1	85	5	naphthalene	92
4-chlorotoluene (10)		1	60	19	toluene	(97)
3-chlorotoluene (10)		1	60	20	toluene	(95)
2-chlorotoluene (10)		1	60	18	toluene	(7)
4-chloroaniline (2)	1.0	5	95	19	aniline	80 (91)
4-chloroanisole (10)		1	80	9.5	anisole	60 (99)
4-chloro(trifluoromethyl)benzene (10)		1	60	18	(trifluoromethyl)benzene	87
3-chlorobenzophenone (5)	1.5	2	50	3	benzophenone benzhydrol	97 <3
p-chlorobenzoic acid (2)	3.0	5	90	25	benzoic acid	99
p-(chlorophenyl)acetic acid (2)	1.0	5	90	21	phenylacetic acid	98
carprofen (0.37)	2.0	10	90	24	α-methyl-9*H*-carbazole-2-acetic acid	91
5-chlorobenzodioxole (1.05)	1.0	10	90	48	benzodioxole	67
5-chloro-1-ethyl-2-methylimidazole (2.1)	1.0	5	80	8	1-ethyl-2-methylimidazole	97
tetrachloro-*m*-xylene (0.5)	1.0	20	100	48	2-chloro-*m*-xylene	45

[a] Isolated yields, except those in parentheses which are yields determined by gas chromatography with an internal standard.

As this system is active enough to catalyze aromatic C–H bond cleavage, it seemed conceivable that hydrogenolysis of the carbon–chlorine bond in chloroarenes could occur by the use of either **1** or **2**. The reduction of chloroarenes to arenes is a useful process, and both stoichiometric reduction and catalytic hydrogenolysis[9] have been used to effect this conversion. For instance, benzene was obtained in good yield from chlorobenzene by using magnesium and 2-propanol.[10] However, this method is not an effective one for the reduction of chloroarenes bearing a variety of substituents including carbonyl, carboxyl, and nitro groups. The only known catalytic methods for dechlorination are heterogeneous in nature. These reactions usually are sensitive to the type of substrate, solvent, platinum metal [Pd, Pt, Rh, Ru], as well as the reaction conditions used.[11] To our knowledge, there are no effective phase-transfer or homogeneous catalytic methods for the hydrogenolysis of the aryl carbon–chlorine bond. We now wish to report a general biphasic and phase-transfer process for the hydrogenolysis of chloroarenes which proceeds under mild conditions and affords products in high yields.

Results and Discussion

Treatment of chlorobenzene with hydrogen in toluene and 40% sodium hydroxide, in the presence of **1** (5 mol %) and benzyltriethylammonium chloride as the phase-transfer agent, afforded benzene in 97% yield (24 h, room temperature, 1 atm). No byproducts were observed in this reaction:

$$RCl + H_2 \xrightarrow[40\%\ NaOH,\ PhCH_2N(C_2H_5)_3{}^+Cl^-]{[(Cy_3P)_2Rh(H)Cl_2],\ PhCH_3} RH$$

The influence of several parameters was examined by using chlorobenzene as the reactant. Lowering the base concentration to 10% NaOH gives benzene in only 55% yield. Chlorobenzene could be used as both reactant and organic phase, with 40% benzene formed when the ratio of PhCl/**1** was 220/1. The yield increased to 50% when a 66/1 ratio of PhCl/**1** was used. Complexes **1** and **2** (gave 95% PhH) exhibit essentially the same catalytic activity, are easy to prepare, and are air stable in the solid state. However, only complex **1** was used in subsequent experiments due to the high relative cost of triisopropylphosphine compared with tricyclohexylphosphine. These reactions are essentially biphasic in nature since the phase-transfer catalyst provides a modest increase in product yield (89% benzene in the absence of the quaternary ammonium salt; 97% using $PhCH_2N(C_2H_5)_3{}^+Cl^-$).

The hydrogenolysis of a variety of substituted chloro aromatic compounds was investigated, and the results are presented in Table I. Chlorobenzenes bearing different electron-donating (e.g. NH_2, OCH_3, CH_3) and electron-withdrawing (e.g. COAr, CF_3, COOH) groups were successfully dechlorinated. For instance, reactions of chlorinated aniline, anisole, (trifluoromethyl)benzene, and benzophenone lead to the corresponding aromatic compounds in almost quantitative yield. The selectivity of these reactions is high with no biaryl formation or aromatic ring hydrogenation observed in any of these reactions. It is noteworthy that a small amount (<3%) of benzhydrol was found in the case of 3-chlorobenzophenone.

It is interesting and important to note that aromatic chloro carboxylic acids undergo smooth dechlorination to give the products in 91–99% isolated yields. One can assume that, under PTC conditions, carboxylate anions are transferred to the organic phase by the quaternary ammonium salt, and the reaction takes place in the organic phase. An interfacial process is also possible, since (4-chlorophenyl)acetic acid afforded phenylacetic acid in 90% yield when the hydrogenolysis catalyzed by **1** was effected in the abfsence of a phase-transfer agent (98% using $PhCH_2N(C_2H_5)_3{}^+Cl^-$). Some chloro heterocycles (e.g. carprofen, chlorobenzodioxole, 5-chloro-1-ethyl-2-methylimidazole) are readily dehalogenated, while 2-chlorothiophene was recovered unchanged on attempted hydrogenolysis.

The reactivity of chloro aromatics is sensitive to steric factors: For instance, 3- and 4-chlorotoluenes possess almost the same reactivity, affording toluene in more than 90% yield. However, reaction of 2-chlorotoluene is rather slow under the same conditions, and toluene was obtained in only 7% yield. Reaction of tetrachloro-*m*-xylene leads to 2-chloro-*m*-xylene and not to *m*-xylene, even at elevated temperature (100 °C) and for an extended reaction time. Therefore, chlorobenzenes with one ortho substituent can be dehalogenated, albeit in low yield, but the presence of two ortho substituents protects the chlorine atom against hydrogenolysis.

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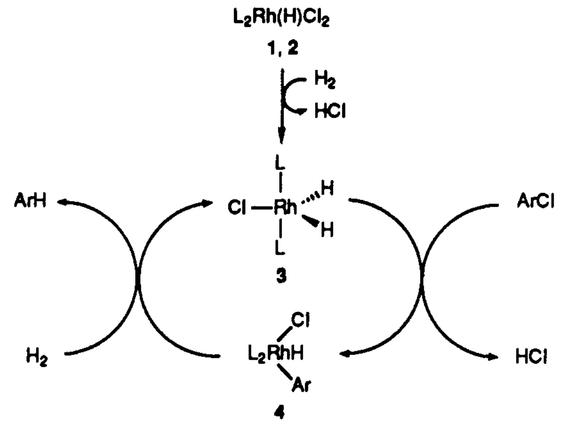
Scheme I



The reaction of aqueous $RhCl_3$ with the appropriate phosphine in refluxing 2-propanol gives **1** and **2**, accompanied by square-planar Rh(II) complexes of formula $[L_2RhCl_2]$.[12-14] The latter non-hydrido Rh(II) species react in a facile manner with hydrogen in solution affording **1** and **2**.[14] Reaction of **2** with H_2 for 3–5 min, under the same PTC conditions, but in the absence of a chloroarene, is known to give **3** in quantitative yield.[7b] This reaction probably proceeds by coordination of hydrogen to rhodium, and then reductive elimination of HCl to give **3**. Equilibration of **1** or **2** with **3** (eq 2)[14] can be shifted to the dihydride by the addition of alkali.[7b] An analogous situation, with the chloroarene playing the role of dihydrogen, may be occurring in the dehalogenation process [Scheme I]. Addition of the chloroarene to **3** followed by elimination of HCl would give the σ-arylhydridorhodium complex **4**. Reductive elimination of arene can then take place, with **3** being regenerated in the presence of H_2. α-Elimination of HCl from **3** under PTC conditions was found to be unlikely even in the absence of ArCl. Prolonged treatment of **3** with H_2 in a KOH/C_6H_6 biphasic system leads to a mixture of hydrido(phosphine)rhodium complexes,[7b,8] some of them being able to activate aromatic C–H bonds.[8] However, the reaction of the resulting clear greenish yellow highly air-sensitive solution with CO (80 °C, 18 h) gave $L_2Rh(CO)Cl$ still containing one chloro ligand (L = i-Pr_3P; 73% isolated yield).

$$\underset{\textbf{1 or 2}}{L_2Rh(H)Cl_2} + H_2 \rightleftarrows \underset{\textbf{3}}{L_2Rh(H)_2Cl} + HCl \qquad (2)$$

In conclusion, the rhodium hydride complexes **1** and **2** are excellent catalysts for the hydrogenolysis of chloroaromatics. The reaction has broad functional group tolerance and occurs in a biphasic manner, with a phase-transfer agent giving somewhat higher product yields.

Experimental Section

General Considerations. Melting point determinations were made with a Fisher-Johns apparatus. Spectral determinations were made by using the following instrumentation: Perkin-Elmer 783 (infrared), Varian XL 300 (nuclear magnetic resonance), and VG 5050 micromass (mass spectra) spectrometers. A Varian 6000 instrument was used for gas chromatographic analysis, with 3% OV-17 on chromosorb W used.

p-Chloroaniline was recrystallized twice from ethanol prior to use. All other chloroarenes were purchased from Aldrich Chemical Co., except 6-chloro-α-methyl-9H-carbazole-2-acetic acid (carprofen) which was obtained from Sigma Chemical Co., and were used as received. Tricyclohexylphosphine (Aldrich), triisopropylphosphine (Strem), aqueous rhodium trichloride (Johnson-Matthey), and hydrogen (Air Products) were also used as received.

Rhodium Catalysts. $[(Cy_3P)_2Rh(H)Cl_2]$, 1. Nitrogen was slowly bubbled, over a 20-min period, through a stirred solution of $RhCl_3$ (1.00 g) in water (2.0 mL) and 2-propanol (40 mL). Tricyclohexylphosphine (4.6 g, 16 mmol) was added and stirring was continued while the reaction mixture was refluxed for 18 h (N_2 atmosphere). Complex **1** was filtered, washed with ethanol (3 × 20 mL), and vacuum dried. The yield of pink-orange **1** was 2.93 g (99%).

$[(i\text{-}Pr_3P)_2Rh(H)Cl_2]$, 2. After N_2 was bubbled for 1 h, through a mixture of 1.01 g of $RhCl_3$ in water (2 mL) and 2-propanol (60 mL), triisopropylphosphine (2.5 mL) was added, and the mixture was refluxed with stirring for 33 h (N_2 atmosphere). Red-orange crystals of **2** were filtered, washed with acetone (2 × 3 mL), and dried in vacuum. The yield of **2** was 1.63 g (82%).

General Procedure for the Rhodium and Phase-Transfer-Catalyzed Hydrogenolysis of Chloroarenes. A solution of NaOH (2.0 g) and benzyltriethylammonium chloride (0.03 g, 0.13 mmol) in 3 mL of H_2O was placed in a 150-mL Schlenk tube. Toluene (if used), the chloroarene, and the rhodium complex (1–10 mol %) were added, and the reaction mixture was immediately degassed by two freeze–pump–thaw cycles. The Schlenk tube was purged with H_2, and the reaction mixture was vigorously stirred under H_2 (see Table I for reaction temperature and time). The organic phase was analyzed by GC with an internal standard. Workup was effected in the following manner (the products were identified by comparison of physical and spectral data with authentic materials).

(a) Naphthalene. Water (10 mL) was added, and the product was extracted with hexane (3 × 20 mL). The combined organic phase was filtered through alumina and concentration of the filtrate gave pure naphthalene.

(b) Anisole and Benzophenone. Pentane (30 mL) was added, and the organic phase was filtered through silica gel, and anisole was obtained on concentration of the filtrate. Benzophenone was worked up in the same way except that benzene (150 mL) was used instead of pentane.

(c) (Trifluoromethyl)benzene. The organic phase was separated, and pure benzotrifluoride was obtained on distillation.

(d) Benzodioxole. Pentane (7.0 mL) was added, the organic phase was separated and concentrated by rotary evaporation. Silica gel thick-layer chromatography of the residue afforded pure heterocycle.

(e) 1-Ethyl-2-methylimidazole. The layers were separated, the aqueous layer was washed with ether (3 × 3 mL), and the ether washings were added to the toluene phase. The combined organic phase was evaporated, and vacuum distillation of the residue gave pure product.

(f) Carboxylic Acids. Water (10–20 mL) was added to the reaction mixture, the aqueous layer was separated, washed with pentane, and acidified with 10% HCl. The product was extracted with ether (3 × 30 mL), dried ($MgSO_4$), and concentrated affording pure carboxylic acid.

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