Catalytic Dehalogenation of Aryl Chlorides Mediated by Ruthenium(II) Phosphine Complexes

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Received August 11, 1998

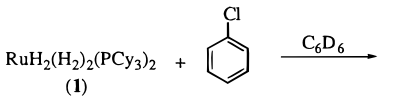
The catalytic dechlorination of aryl chlorides performed by $RuHCl(H_2)_2(PCy_3)_2$ and $RuH_2(H_2)_2(PCy_3)_2$ in alcohols is rapid and complete within 1 h. The mechanism involves a transfer hydrogenation step with participation of the alcohol. The system exhibits significant functional group tolerance. The catalyst can be generated *in situ* from $[RuCl_2(COD)]_x$ (COD = cyclooctadiene) and 2 equiv of phosphine (PCy_3 or P^iPr_3). Catalytic conversions are similar to those observed when an isolated precatalyst is used. Mechanistic considerations and the scope of the process are discussed.

Introduction

Chloroarenes are of particular interest because of their deleterious environmental and health impact[1] as well as their importance in organic synthesis.[2] Environmental concerns have driven researchers to examine practical and effective processes for the reduction of highly toxic chloroarenes into arenes. The high stability of the aryl carbon−chlorine bond renders it less reactive compared to other aryl−halogen bonds in many organic transformations and reactions.[2] It is with this chemical resiliency and potential carcinogenicity in mind that we directed our efforts toward the transformation of C−Cl bonds.

Several methods for hydrogenolysis of chloroarenes, using either stoichiometric and/or catalytic reagents, have been developed by Imai (Pd),[3] Carfagna (Ni),[4] Qian (La),[5] Horváth (Rh),[6] and Alper (Rh),[7] among others.[8] However, these systems can still be improved, as most suffer from incomplete dechlorination, low catalytic activity, low substrate/catalyst ratio, extreme conditions (high H_2 pressure, long reaction times), or narrow functional group tolerance.

Ruthenium hydride complexes are useful as precursors to ruthenium carbenes[9,10] as well as active hydrogenation catalysts.[11−14] Interest in ruthenium complexes has grown due to their tolerance toward oxygen, protic solvents, and a variety of functional groups. During earlier work in our group,[9] the formation of $RuHCl(H_2)_2(PCy_3)_2$ (**2**) by reaction of $RuH_2(H_2)_2(PCy_3)_2$ (**1**) and chlorobenzene was observed (eq 1).



$RuH_2(H_2)_2(PCy_3)_2$ (**1**) + → $RuHCl(H_2)_2(PCy_3)_2$ (**2**) + (1)

A similar reaction reported by Chaudret and coworkers was the observation by NMR that **1** readily reacted with dichloromethane, leading to the formation of **2**.[15] These reactions prompted interest in investigating the catalytic activity of **1** with chloroarenes. We have recently reported convenient synthetic routes leading to the isolation of $RuH_2(H_2)_2(PCy_3)_2$ (**1**)[9] and $RuHCl(H_2)_2(PCy_3)_2$ (**2**)[10] from readily available materials in high yields; therefore, we were interested in exploring the potential use of these ruthenium hydride complexes as dechlorination catalysts. We now report the rapid and complete catalytic reduction of chloroarenes to arenes using Ru(II) catalysts, without a need for hydrogen gas.

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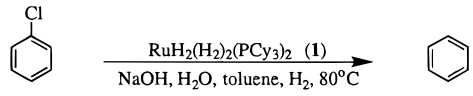
(1) Hutzinger, O.; Safe, S.; Zitko, V. *The Chemistry of PCBs*; CRC Press: Cleveland, OH, 1974.
(2) (a) March, J. *Advanced Organic Chemistry*; Wiley-Interscience: New York, 1992. (b) Imamoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: London, 1991; Vol. 8, p 793. (c) Hudlicky, M. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: London, 1991; Vol. 8, p 895.
(3) Imai, H.; Nishiguchi, T.; Tanaka, M.; Fukuzumi, K. *Chem. Lett.* **1976**, 855−856. Imai, H.; Nishiguchi, T.; Tanaka, M.; Fukuzumi, K. *J. Org. Chem.* **1977**, *42*, 2309−2313.
(4) Carfagna, C.; Musco, A.; Pontellini, R. *J. Mol. Catal.* **1989**, *54*, L23−L26.
(5) Qian, C.; Zhu, D.; Gu, Y. *J. Mol. Catal.* **1990**, *63*, L1−L3.
(6) Ferrughelli, D. T.; Horváth, I. T. *J. Chem. Soc., Chem. Commun.* **1992**, 806−807.
(7) (a) Grushin, V. V.; Alper, H. *Organometallics* **1991**, *10*, 1620−1622. (b) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047−1062.
(8) Love, C. J.; McQuillin, F. J. *J. Chem. Soc., Perkin Trans.* **1973**, 2509−2512.
(9) Belderrain, T. R.; Grubbs, R. H. *Organometallics* **1997**, *16*, 4001−4003.
(10) (a) Wilhelm, T. E.; Belderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867−3869. (b) Olivan, M.; Caulton, K. G. *J. Chem. Soc., Chem. Commun.* **1997**, 1733−1734.
(11) Saburi, M.; Takeuchi, H.; Ogasawa, M. T.; Tsukahara, Y. I.; Ikariya, T.; Takahashi, T. *J. Organomet. Chem.* **1992**, *428*, 155−167.
(12) Schlaf, M.; Lough, A. J.; Morris, R. H. *Organometallics* **1997**, *16*, 1253−1259.
(13) Albers, M. O.; Singleton, E.; Viney, M. M. *J. Mol. Catal.* **1985**, *33*, 77−82.
(14) Saburi, M.; Ohnuki, M.; Ogasawa, M. T.; Takahashi, T.; Uchida, Y. *Tetrahedron Lett.* **1992**, *33*, 5783−5786.
(15) Christ, M.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1994**, *13*, 3800−3804.

10.1021/om980682n CCC: $18.00
Publication on Web 03/12/1999

Results and Discussion

Dechlorination with $Ru(H)(X)(H_2)_2(PCy_3)_2$ (X = H, Cl) under H_2. Conditions similar to those employed for the synthesis of **1** were used as a starting point in the dechlorination studies with complex **1** as the catalyst precursor. More specifically, the conversion of chlorobenzene to benzene was performed using 1 mol % of catalyst **1** and 30% (by weight) aqueous sodium hydroxide solution, under 3 atm of H_2 at 80 °C in toluene (eq 2). Under these conditions, GC analysis showed that conversion to benzene was efficient but not complete.



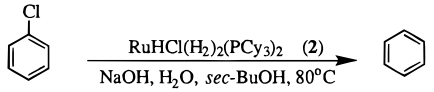
(2)

Further studies showed that **1** could be prepared from **2** under strong basic conditions (eq 3).

$$\underset{\mathbf{2}}{RuHCl(H_2)_2(PCy_3)_2} \xrightarrow{[NaOH]} \underset{\mathbf{1}}{RuH_2(H_2)_2(PCy_3)_2} \quad (3)$$

This result led us to consider the use of **2** as a catalyst for the dechlorination of aryl chlorides. This would provide a number of synthetic advantages, since **2** is easier to isolate and is more stable than **1**. In fact, complex **2** can also convert chlorobenzene to benzene, using the same conditions as those described in eq 2. Complex **2** was subsequently used as the catalyst precursor.

Dechlorination with $Ru(H)(X)(H_2)_2(PCy_3)_2$ (X = H, Cl) without H_2. In an effort to improve/simplify catalytic conditions, solvent effects on catalytic conversions were investigated. Since the system utilizes biphasic conditions, it was important to examine whether changing the solvent or using a phase transfer catalyst could improve conversions by enhancing the interaction between the aqueous and organic phases. Changing the solvent from toluene to *sec*-butyl alcohol resulted in improved catalytic activity under a hydrogen atmosphere. Simultaneously in our group, efforts directed toward the syntheses of ruthenium hydride complexes showed that a secondary alcohol could provide an efficient hydrogen source and that molecular hydrogen was not needed and indeed was often an impediment to the isolation of ruthenium hydride complexes.[16] Transfer hydrogenation mediated by transition-metal centers (including ruthenium) has been reported by other groups.[17−22] This prompted investigation of the use of a secondary alcohol, *sec*-butyl alcohol, as the solvent in the dechlorination of chloroarenes in the absence of hydrogen gas (eq 4).



(4)

Indeed, the conversion of chlorobenzene proceeds efficiently and cleanly in the absence of hydrogen gas. In fact, the conversion efficiency is significantly higher in the absence of H_2. It appears that H_2 has a retarding effect on catalytic activity, as has been reported in other hydrogen-transfer systems.[23] The concentration of the base on catalytic activity was also investigated to determine whether more basic conditions would improve conversions. Only a modest improvement in conversions was observed when increasing the base concentration from 30% to 50%.[24] In an effort to further optimize catalytic conditions, the catalyst loading was increased from 1% to 2.5%. As expected, the conversion efficiency greatly improved with the higher catalyst loading from 49% (with 1% catalyst) to 100% (with 2.5% catalyst) under identical conditions. After optimum catalytic conditions were determined, a variety of chloroarene substrates were investigated. All are quantitatively converted to dechlorinated products after 1 h at 80 °C. The dechlorination results are summarized in Table 1.

Importantly, the catalytic system displays tolerance toward substrates bearing functional groups such as ketones, ethers, and pyridines. Moreover, multichlorinated arenes are completely dechlorinated.[25]

In Situ Catalyst Generation from $[RuCl_2(COD)]_x$. Since **1** and **2** can be synthesized from the air-stable $[RuCl_2(COD)]_x$ (**3**), hydrogenolysis of chloroarenes was examined by in situ generation of the catalyst precursor. This methodology is advantageous, as it does not require the isolation of the catalyst precursor, enabling dechlorination to be carried out in a "one pot" reaction. To verify the need of dihydrogen in the generation of the *in situ* catalyst complex, side by side reactions were conducted in the absence and presence of dihydrogen:

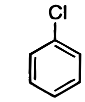
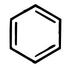
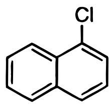
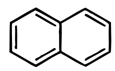
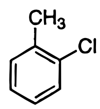
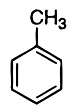
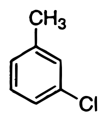
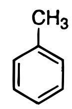
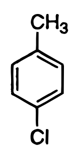
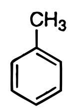
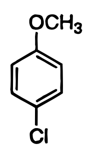
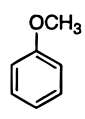
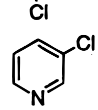
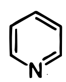
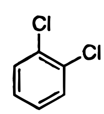
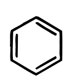
$$\underset{\mathbf{3}}{[RuCl_2(COD)]_x} + 2PCy_3 \xrightarrow[\text{(2) R−Cl addition under Ar, 80 °C}]{\text{(1) NaOH, } H_2O\text{, } sec\text{-BuOH, 80 °C}} \text{dark red solution} \quad (5)$$

$$\underset{(\mathbf{3})}{[RuCl_2(COD)]_x} + 2PCy_3 \xrightarrow[\text{2. R-Cl addition under Ar, 80 °C}]{\text{1. NaOH, } H_2O\text{, } sec\text{-BuOH, } \mathbf{H_2}\text{, 80 °C}} \text{orange solution} \quad (6)$$

In the absence of hydrogen (eq 5), the species generated is neither **1** nor **2** but a close parent, $Ru(\eta^3\text{-}C_6H_8\text{-}PCy_2)(PCy_3)Cl$ (**4**), which has been reported to hydrogenate nitrile substrates.[26] Since complex **4** can be readily converted to complex **2**,[26] it follows that both **2** and **4** are likely entry points into the catalytic cycle. The

(16) Nolan, S. P.; Belderrain, T. R.; Grubbs, R. H. *Organometallics* **1997**, *16*, 5569−5571.
(17) Akamanchi, K. G.; Varalakshmy, N. R. *Tetrahedron Lett.* **1995**, *36*, 3571−3572 and references cited therein.
(18) (a) Müller, D.; Umbricht, G.; Weber, B.; Pfaltz, A. *Helv. Chim. Acta* **1991**, *74*, 232−240. (b) Evans, D. A.; Nelson, S. G.; Muci, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 9800−9801. (c) Genêt, J. P.; Ratovelomanana-Vidal, V.; Pinel, C. *Synlett* **1993**, 478−480.
(19) (a) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994 and references therein. (b) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97−102.
(20) Vincente, C.; Shul'pin, G. B.; Moreno, B.; Sabo-Etienne, S.; Chaudret, B. *J. Mol. Catal. A: Chem.* **1995**, *98*, L5−L8.
(21) Transfer hydrodehalogenation of alkyl chlorides mediated by water-soluble Ru(II) phosphine complexes has recently been reported: Benyei, A. C.; Lehel, S.; Joo, F. *J. Mol. Catal. A: Chem.* **1997**, *116*, 349−354.
(22) Gamez, P.; Fache, F.; Lemaire, M. *Tetrahedron: Asymmetry* **1995**, *6*, 705−718.
(23) Bianchini, C.; Farnetti, E.; Graziani, M.; Peruzzini, M.; Polo, A. *Organometallics* **1993**, *12*, 3753−3761.
(24) Conversion efficiency was improved by an average of less than 5% when a higher NaOH concentration was used.
(25) Complete conversion of trichlorobenzene to benzene was performed, using catalytic conditions similar to those above, in 2 h.
(26) Beatty, R. P.; Paciello, R. A. U.S. Patent 5,444,778, 1996.

Table 1. Catalytic Dehalogenation with $RuHCl(PCy_3)_2(H_2)_2$ in *sec*-Butyl Alcohol[a]

Substrate	Product	Cat. mol %	Time (h)	% Converted[a]
		2.5	1	100
		2.5	1	100
		2.5	1	100
		2.5	1	100
		2.5	1	100
		2.5	1	100
		2.5	1	100
		2.5	1	100

[a] Percent conversions determined by GC.

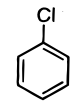
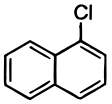
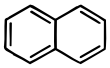
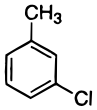
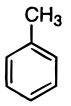
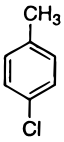
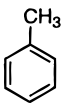
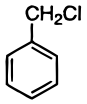
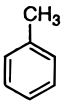
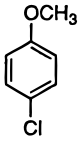
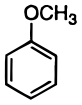
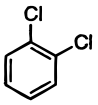
catalytic solutions obtained according to eq 5 do perform catalytic dehalogenation, but significant amounts of decompositions are observed upon generation of these solutions. Their catalytic efficiency is lower than solutions generated according to eq 6, which appear to benefit from the stabilizing effect of having dihydrogen as a labile ligand.

The effect of temperature on percent conversion was investigated for chlorobenzene with the *in situ* generated catalyst **4** in the absence of H_2 (see the Supporting Information for a temperature vs percent conversion plot). Increasing temperature leads to greater conversion efficiency, with a maximum reached at 80 °C. However, above this temperature, the homogeneous solution displays signs of catalyst decomposition. The reactivity of the catalytic species formed from **3** is comparable to that displayed by the isolated catalyst **1** or **2**. The catalytic results involving **3** are presented in Table 2.

The isolated catalysts **1** and **2** give slightly better conversions, suggesting that a small percentage of the starting material may not be converted into active catalytic species. The pyridine derivative may significantly bind to the synthetic precursor **3**, hindering formation of the active catalyst. The rate of dechlorination of chlorobenzene using **2** was monitored by GC analysis of aliquots taken from the reaction mixture at known time intervals. A first-order rate constant of 1.8×10^{-3} s^{-1} can be calculated for the conversion, which corresponds to $t_{1/2} = 6.4$ min. The kinetic plot is provided in the Supporting Information.

Dechlorination with $Ru(H)Cl(H_2)_2(P^iPr_3)_2$. The efficiency and activity of the dechlorination reaction was tested as a function of the nature of the phosphine ligand bound to the ruthenium center. Using experimental reaction conditions identical with those in eq 7, reaction of $[RuCl_2(COD)]_x$ (**3**) with 2 equiv of P^iPr_3 leads to the formation of $RuHCl(H_2)_2(P^iPr_3)_2$ (**5**).[10]

Table 2. Catalytic Dehalogenation with $[RuCl_2(COD)]_x$ + 2PCy_3 in *sec*-Butyl Alcohol and H_2[a]

Substrate	Product	Cat. mol %	Time (h)	% Converted[a]
		2.5	1	99
		2.5	1	96
		2.5	1	95
		2.5	1	89
		2.5	1	92
		2.5	1	95
		2.5	1	81
		2.5	1	35

[a] Percent conversions determined by GC.

$$[RuCl_2(COD)]_x + 2P^iPr_3 + NEt_3 \xrightarrow[H_2]{sec\text{-}BuOH} [Ru(H)(Cl)(H_2)_2(P^iPr_3)_2] + HNEt_3Cl + C_8H_{16} \quad (7)$$

5

Utilization of **5** in catalytic dechlorination experiments leads to complete conversion of chlorobenzene to benzene. Catalytic conversions are the same as those performed using **1** or **2**.

Proposed Mechanism. From the available experimental evidence, a simple mechanism based on transfer hydrogenation chemistry is proposed. The catalytic cycle is illustrated in Scheme 1.

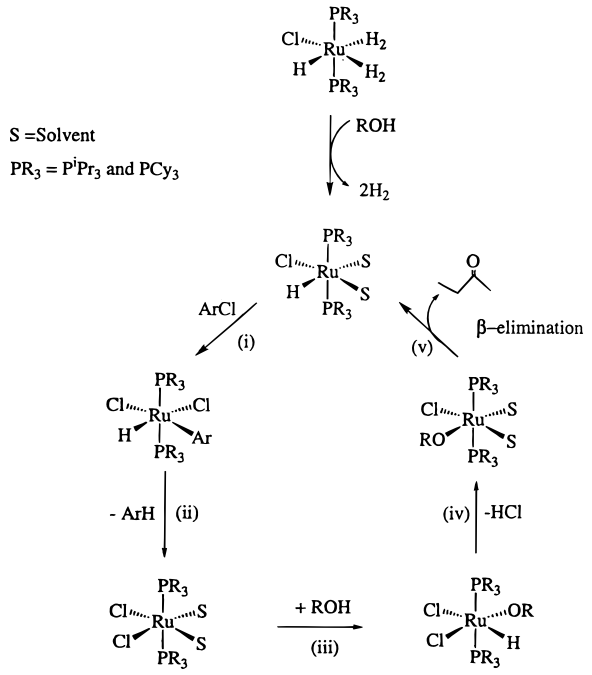
In the first step (i), a ruthenium(II) species oxidatively adds the aryl chloride, leading to the formation of a ruthenium(IV) complex. In the second step (ii), the arene is reductively eliminated from the coordination sphere of the metal, leading to the formation of a ruthenium dichloro species which then undergoes oxidative addition of the alcohol to form a ruthenium(IV) complex (step iii). This species then releases HCl (driven by the presence of the base), leading to an alkoxychlororuthenium species. β-Hydride elimination from the alkoxy ligand, liberating the ketone, regenerates the initial catalytic species.

Hydrogen transfer reactions of alkoxides, or alcohols in the presence of NaOH, with ruthenium halide complexes are well-known methods for the preparation of ruthenium hydrides.[27] 2-Butanone, the ketone generated in step iv, was detected by GC in every dechlorination experiment carried out in *sec*-butyl alcohol. If a nonsecondary alcohol is used, such as methanol or *tert*-butyl alcohol, no conversion occurs. The formation of ruthenium carbonyl complexes via decarbonylation of methanol has previously been reported. This specific need for a secondary alcohol was tested by using 2-propanol as the solvent. Efficient conversions are observed, as in experiments involving *sec*-butyl alcohol.

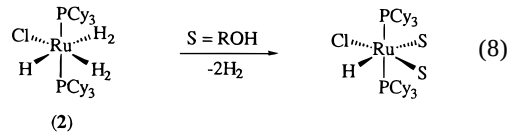
A number of entry ways into the catalytic cycle are possible. It has already been stated that complexes **1**

(27) (a) Chatt, J.; Shaw, B. L.; Field, A. E. *J. Chem. Soc.* **1964**, 3466. (b) Chaudret, B.; Cole-Hamilton, D. J.: Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546. (c) Chaudret, B.; Poilblanc, R. *Inorg. Chim. Acta* **1979**, *24*, 2209. (d) Lupin, M. S.; Shaw, B. L. *J. Chem. Soc. A* **1968**, 741.

Scheme 1. Proposed Mechanism for Ruthenium-Mediated Catalytic Dehalogenation



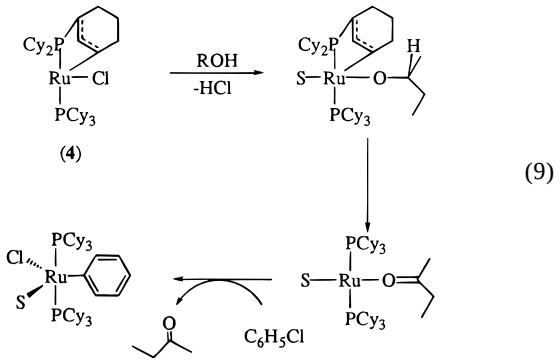
and **2** can be interconverted. We therefore consider them as a single entry point. Simple loss of its dihydrogen ligands in the presence of alcohol solvent converts **2** into the initial catalytic species:



(8)

(**2**)

The *in situ* catalyst generation reaction leads to **1** or **2** if dihydrogen is used in the precatalyst formation reaction. The independently synthesized complex Ru(η^3-C_6H_8-PCy_2)(PCy_3)Cl (**4**) can also be used as a catalyst precursor and may be one of the intermediates involved in the course of the in situ catalyst generation. Since **4** is easily converted into **1** under hydrogen in basic media, we consider it as an alternative entry way into the catalytic cycle:



(**4**)

(9)

Conclusion

$RuH_2(H_2)_2(PCy_3)_2$ (**1**) and $RuHCl(H_2)_2(PCy_3)_2$ (**2**) prove to be excellent catalysts for the dechlorination of chloroarenes. The reactions are complete after 1 h. Most notably, the reactions are performed in the absence of dihydrogen. The dechlorination proceeds via transfer hydrogenation. The catalysts are tolerant of a variety of functional groups and are efficient in dechlorinating multichlorinated arenes. The catalytic species may be generated *in situ* from the air-stable precursor $[RuCl_2(COD)]_x$ (**3**), and conversions obtained using **3** are comparable to those obtained using the isolated catalyst **2**. The catalyst lifetime/activity was tested by subsequent addition of substrate and showed constant conversion efficiency. The experimental results, especially the identification of the ketone generated in the course of the reaction,[28] lend support to the proposed mechanism, which involves transfer hydrogenation using secondary alcohols as the hydrogen source.

Experimental Section

General Procedures. All manipulations were carried out using standard high-vacuum or Schlenk techniques under an atmosphere of argon. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4 Å molecular sieves. Solids were transferred and stored in a nitrogen-filled Vacuum Atmospheres drybox. ^1H and ^{31}P NMR spectra were recorded on a JEOL GX 400 MHz (399.1 MHz, ^1H; 161.9 MHz, ^{31}P) spectrometer at 20 °C. Gas chromatographic analyses were performed on a Hewlett-Packard Model 5890 Series II GC equipped with an SE 30 capillary column. Identities of reaction components were determined by comparison with commercial samples by gas chromatography.

Materials. Chloroarenes, arene products, and 2-butanone were purchased from Aldrich. The organometallic complexes $RuH_2(H_2)_2(PCy_3)_2$ (**1**),[9,10] $RuHCl(H_2)_2(PCy_3)_2$ (**2**),[10] $[RuCl_2(COD)]_x$ (**3**),[29] and $RuHCl(H_2)_2(P^iPr_3)_2$ (**5**)[10] were synthesized according to literature procedures. *sec*-Butyl alcohol, methanol, 2-propanol, and *tert*-butyl alcohol were purchased from Aldrich as anhydrous grade (99.5%) and purged with Ar prior to use. Toluene and deuterated benzene were purified using procedures previously reported.[30] $RuCl_3 \cdot xH_2O$, $RhCl_3 \cdot xH_2O$, PCy_3, and P^iPr_3 were purchased from Strem and used as received.

General Procedure for the $Ru(H)(Cl)(H_2)_2(PCy_3)_2$-Catalyzed Dehalogenations of Chloroarenes. A 500 mL Fisher−Porter bottle was charged with $Ru(H)(Cl)(H_2)_2(PCy_3)_2$ (**2**; 100 mg, 0.14 mmol). Degassed *sec*-butyl alcohol (40 mL) and 50% NaOH solution (15 mL) were then transferred by cannula into the reaction vessel. The chloroarene substrate (5.6 mmol) was added by syringe, and the reaction vessel was then closed and heated to 80 °C for 1 h. After the mixture was cooled to room temperature, an aliquot was removed from the organic phase and filtered through a silica gel−glass wool plug loaded in a disposable pipet. The filtrate was then analyzed by GC using an internal standard.

General Procedure for the in Situ Catalyzed Dehalogenations of Chloroarenes from $[RuCl_2(COD)]_x$. A 500 mL Fisher−Porter bottle was charged with $[RuCl_2(COD)]_x$ (**3**; 100 mg, 2.5 mmol) and 2 equiv of PR_3 (R = cyclohexyl, isopropyl). Degassed *sec*-butyl alcohol (40 mL) and 50% NaOH solution (15 mL) were transferred by cannula into the reaction container. The reaction mixture was then pressurized to 3 atm of H_2. The reaction vessel was subsequently closed and heated

(28) Since Rh complexes have been shown to perform transfer hydrogenations,[22] we found that the Rh system, $[RhL_2(H)Cl_2]$ (L = PCy_3, P^iPr_3) gave complete dechlorination of aromatic chlorides without dihydrogen when a secondary alcohol was used as the solvent.

(29) Albers, M. O.; Ashworth, T. V.; Oosthuizen, E.; Singleton, E. *Inorg. Synth.* **1989**, *26*, 68−77.

(30) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

to 80 °C for 3 h. Prior to addition of the chloroarene substrate, the reaction vessel was cooled to room temperature and was purged for 20 min under a flow of argon. Next, the chloroarene substrate was added (100 mmol) and the reaction vessel was again heated to 80 °C for 1 h. After the mixture was cooled, an aliquot, taken from the organic phase, was filtered through a silica gel−glass wool plug in a disposable pipet. The filtrate was analyzed by GC with an internal standard. Upon further substrate addition and heating at 80 °C, conversions of chloroarenes to arenes were determined to proceed quantitatively.

Acknowledgment. The National Science Foundation is gratefully acknowledged for support of this work.

Supporting Information Available: Figures giving plots of the conversion of chlorobenzene to benzene vs reaction temperature using in situ generated catalyst without dihydrogen and of the reaction kinetics at 80 °C for dehalogenation of chlorobenzene to benzene. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980682N