Complete Hydrodehalogenation of Polyfluorinated and Other Polyhalogenated Benzenes under Mild Catalytic Conditions

3 **AUTHORS**, INCLUDING:

Rebekka Baumgartner
ETH Zurich
5 PUBLICATIONS **223** CITATIONS

SEE PROFILE

Kristopher McNeill
ETH Zurich
**126** PUBLICATIONS **3,415** CITATIONS

SEE PROFILE

Complete Hydrodehalogenation of Polyfluorinated and Other Polyhalogenated Benzenes under Mild Catalytic Conditions

Rebekka Baumgartner, Greta K. Stieger, and Kristopher McNeill*

Institute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, 8092 Zurich, Switzerland

Ⓢ *Supporting Information*

ABSTRACT: Polyfluorinated arenes are increasingly used in industry and can be considered emerging contaminants. Environmentally applicable degradation methods leading to full defluorination are not reported in the literature. In this study, it is demonstrated that the heterogeneous catalyst Rh/Al_2O_3 is capable of fully defluorinating and hydrogenating polyfluorinated benzenes in water under mild conditions (1 atm H_2, ambient temperature) with degradation half-lives between 11 and 42 min. Analysis of the degradation rates of the 12 fluorobenzene congeners showed two trends: slower degradation with increasing number of fluorine substituents and increasing degradation rates with increasing number of adjacent fluorine substituents. The observed fluorinated intermediates indicated that adjacent fluorine substituents are preferably removed. Besides defluorination and hydrogenation, the scope of the catalyst includes dehalogenation of polychlorinated benzenes, bromobenzene, iodobenzene, and selected mixed dihalobenzenes. Polychlorobenzene degradation rates, like their fluorinated counterparts, decreased with increasing halogen substitution. In contrast to the polyfluorobenzenes though, removal of chlorine substituents was sterically driven. All monohalobenzenes were degraded at similar rates; however, when two carbon—halogen bonds were in direct intramolecular competition, the weaker bond was broken first. Differences in sorption affinities of the substrates are suggested to play a major role in determining the relative rates of transformation of halobenzenes by Rh/Al_2O_3 and H_2.
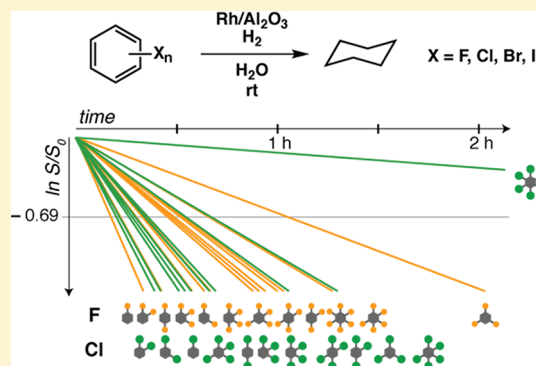
INTRODUCTION

Transition-metal-mediated dehalogenation of aromatic compounds is a reaction of interest from both synthetic and environmental chemistry perspectives. Studies of C−Cl and C−F activation have led to important tools for selective functionalization of organic molecules.[1,2] From an environmental perspective, carbon−halogen activation is important, as halogenated aromatics are ubiquitous and persistent pollutants. Chloroarenes have been widely produced and used since the middle of the 20th century, and as a result they are widespread environmental contaminants. Supported transition-metal-mediated chloroarene dehalogenation has been a focus of many studies, resulting in a variety of catalysts that are suitable for environmental applications.[3]

Fluoroarenes are not as well known or widespread as chloroarenes but can be considered emerging contaminants. The estimated global production capacity of the most important fluoroaromatics was 35 000 tons per year in 2000,[4] and trends in the past[5] indicate a further increase in production and use since 2000. They are used as intermediates in the fluorochemical industry and are an increasingly common structural motif in many pharmaceuticals.[4,6] Therefore, they are expected to enter the environment through industrial spills or wastewater discharge. In the environment, they are relatively persistent due to the high stability of the C−F bond.[5] Indeed,

fluorobenzene has been found in groundwater close to an abandoned industrial site at concentrations up to 700 μg L^{-1},[7] and fluorinated pharmaceuticals are frequently detected in both influents and effluents of sewage treatment plants.[8,9]

We have previously shown that fluorobenzene can be catalytically degraded under environmentally relevant conditions (in water, room temperature, 1 atm of H_2) in the presence of Rh/Al_2O_3 catalyst to form cyclohexane and fluoride.[10] The underlying mechanistic principles were investigated, and a degradation pathway was proposed involving initial defluorination to form benzene, followed by stepwise hydrogenation to cyclohexane. For the present study, we were interested in whether the scope of the catalytic Rh-based system could be extended to polyfluorinated benzenes and other halogenated benzenes.

Polyfluorobenzenes have high C−F bond energies, which make them challenging to degrade. Previously reported degradation reactions for polyfluorinated arenes often do not lead to full defluorination, a necessary criteria for remediation. Early work by Aizenberg and Milstein demonstrated that

rhodium silyl complexes were capable of removing one fluorine substituent from hexa- and pentafluorobenzene under mild conditions.[11] Since then, defluorination has been achieved with other Rh-based catalysts,[12−15] as well as with nickel,[16−20] palladium,[21] platinum,[22] iron,[23] ruthenium,[24] gold,[25] or mixed-metal[26] (Rh/Pd) catalysts. Among these, only the Ni-based catalytic reaction of Wu and Cao[19] was shown to fully defluorinate hexafluorobenzene, whereas in all other studies, fluorinated products remained. Furthermore, none of the above-cited catalytic systems are suitable for application to remediation of contaminated water, as none of the reactions were performed in water, and most of them work only under elevated temperature or hydrogen pressure conditions.

Previous investigations of fluorobenzene activation have illustrated the difficulty in developing a catalyst that can efficiently degrade monofluorinated as well as polyfluorinated benzenes. Monofluorinated benzenes can be degraded catalytically using a range of catalysts under a variety of conditions.[12−15,17,19,21,22,27−29] Among the catalysts that were shown to catalytically defluorinate monofluorinated benzenes, some were also shown to degrade other halogenated benzenes,[12,13,21,27] but only a few also catalyzed hydrodefluorination of higher fluorinated benzenes.[19,28,29]

Limited scope is also a problem for biodegradation of fluorinated benzenes. Fluorobenzene is degraded by a number of microbiological systems,[30−33] but only one study has shown difluorobenzene degradation.[34] To our knowledge, biodegradation of higher fluorinated benzenes has not yet been observed.

Here, we report that the heterogeneous catalyst system of Rh/Al$_2$O$_3$ and H$_2$ in water is capable of full defluorination of all congeners of fluorinated benzenes under mild conditions and at rates on the same order of magnitude as the rate of fluorobenzene degradation in the same system. Furthermore, we show that all chlorobenzene congeners, as well as other halogenated benzenes, can be degraded in the same system. Preferential susceptibility of the different carbon−halogen bonds to the hydrodehalogenation by the catalyst was determined. Rates and intermediates formed were used to generate mechanistic hypotheses.

■ MATERIALS AND METHODS

Reagents. Details on gases and authentic standards are given in the Supporting Information.

Catalyst. The catalyst material, 5% Rh by weight on γ-Al$_2$O$_3$ (Rh/Al$_2$O$_3$), was purchased from Sigma-Aldrich. Manufacturer-specified metal weight was assumed to be accurate. The BET surface was 150.7 m^2 g^{-1}, determined by N$_2$ adsorption (Quantachrome Autosorb). The mean diameter of the catalyst particles was 55 μm (Horiba LA-950 Laser Scattering Particle Size Distribution Analyzer). Transmission electron microscope (TEM) analysis was performed on a CM12 microscope (Philips) with a 100 kV acceleration voltage. Rh particle size distribution was estimated by statistical analysis on approximately 270 Rh particles; Rh particles on the Al$_2$O$_3$ support had an average diameter of 2.7 nm. Rhodium dispersion, defined as the molar ratio between surface metal and bulk metal, was estimated from TEM particle size distribution and approximately 45%. TEM images are shown in the Supporting Information. Characterization showed that the catalyst was similar but not identical to those studied by Hornstein et al.[35] No special precautions were taken to avoid exposure to air prior to the batch experiments.

Batch Experiments. *General Procedure.* Batch experiments were performed in glass bottles (246 mL) sealed with crimp caps lined with rubber septa in buffered Milli-Q water (164 mL, pH 7, 0.01 M phosphate buffer) at room temperature (21 °C ± 2). Buffer was used to prevent the slight decrease in pH observed in the unbuffered system and shown to not affect the determined rate constants. The solution was sparged with H$_2$ for 15 min prior to initiation of the reaction and kept under constant H$_2$ pressure during the course of the reaction (1 atm). Starting materials and (internal) standards, α,α,α-trifluorotoluene or 4-chlorotoluene and 1,2-dichloroethane, were individually added by syringe through the septum to provide the initial compound concentrations. The system was equilibrated for 15 min under constant stirring. Rh/Al$_2$O$_3$ (1.89 mg$_{Rh}$ L^{-1}) was added in powder form using a glass syringe by rinsing it with the reaction solution. Vigorous stirring was continued during the reaction to limit mass transfer effects. Headspace samples (100 μL) were taken at defined time points using a gastight syringe (500 μL) and directly injected into the gas chromatograph. For the chlorobenzenes, bulk-phase samples were taken in addition to the headspace samples. Aliquots of 100 μL were sampled with a glass syringe and added to 50 μL of hexane in a HPLC vial with flat-bottom insert. Vials were immediately closed and agitated with a vortex mixer to allow the chlorobenzenes to partition into the hexane. Due to the efficiency of the extraction, water samples did not require filtration.

Spike Levels. Fluorinated benzenes, mixed halogenated benzenes, and unhalogenated benzene derivatives were directly spiked from the purchased standards at initial concentrations of 100 μM. Initial compound concentrations of the chlorobenzenes were adapted to the linear range of the analytical method and substance solubilities and were 5 μM for chlorobenzene and di- and trichlorobenzenes, 2 μM for tetrachlorobenzenes and pentachlorobenzene, and 1 μM for hexachlorobenzenes. Chlorobenzenes were spiked from stock solutions prepared in THF (10 or 20 mM). Batch experiments were performed twice for each starting material, with several days in between the experiments in each case.

Internal Standards. Two kinds of standards were applied. (1) The reactive standard degraded with Rh/Al$_2$O$_3$ and H$_2$ at a similar rate compared to the target substances. Normalization of the degradation rate constants to the degradation rate constant of the reactive standard corrected for daily variations in the performance of the catalyst and for errors in the handling of the catalyst. The rate constants of the target substances were not significantly affected by addition of the reactive standards. In batch experiments of the fluorinated and unhalogenated benzenes, the reactive standard was α,α,α-trifluorotoluene (100 μM), which was converted to trifluoromethylcyclohexane. 4-Chlorotoluene (20 μM) was the reactive standard for the chlorinated and mixed halogenated benzenes, and it was converted to methylcyclohexane. (2) The (unreactive) internal standard (IS), 1,2-dichloroethane, was only used for batch experiments with chlorinated benzenes. It was found to be stable under the applied reaction conditions and corrected for errors during handling of the sample, extraction, and other aspects of the analytical procedure.

Analytical Methods. Gas chromatography coupled to mass spectrometry (GC-MS) was used for analysis of the headspace samples and GC-ECD (electron capture detector) for the bulk samples. Details for the instruments, methods, and procedures are given in the Supporting Information. Limits of detection

Table 1. Pseudo-First-Order Rate Constants (k_{obs}), Rate Constants Normalized to the Reactive Standard (k_{rel}), Rate Constants Normalized to the Reactive Standard and to the Respective Monohalogenated Benzene ($k_{rel,norm}$), and Half-Lives ($t_{1/2}$, based on k_{obs}) for All Tested Substances[a]

| | Fluorobenzenes | | |
| | Rh: 1.89 mg_{Rh} L^{-1} | IS: α,α,α-trifluorotoluene | | |
	k_{obs} [h^{-1}]	k_{rel} [−]	$k_{rel,norm}$ [−]	$t_{1/2}$ [min]
fluorobenzene (FB)	3.7 ± 0.8	2.7 ± 0.3	1.00 ± 0.12	11 ± 2.4
1,2-diFB	3.0 ± 0.8	2.8 ± 0.3	1.04 ± 0.13	14 ± 3.6
1,3-diFB	1.9 ± 0.3	1.8 ± 0.2	0.67 ± 0.08	22 ± 3.0
1,4-diFB	2.2 ± 0.5	2.0 ± 0.1	0.74 ± 0.05	19 ± 4.7
1,2,3-triFB	2.0 ± 0.7	2.3 ± 0.5	0.87 ± 0.19	21 ± 7.1
1,2,4-triFB	1.3 ± 0.3	1.7 ± 0.1	0.62 ± 0.03	33 ± 8.6
1,3,5-triFB	0.6 ± 0.3	0.8 ± 0.2	0.31 ± 0.08	67 ± 32
1,2,3,4-tetraFB	1.5 ± 0.2	1.9 ± 0.3	0.73 ± 0.11	29 ± 4.1
1,2,3,5-tetraFB	1.4 ± 0.1	1.2 ± 0.1	0.44 ± 0.02	30 ± 2.5
1,2,4,5-tetraFB	1.3 ± 0.5	1.4 ± 0.2	0.51 ± 0.07	31 ± 11
pentaFB	1.0 ± 0.5	1.6 ± 0.4	0.61 ± 0.15	42 ± 22
hexaFB	1.2 ± 0.1	1.6 ± 0.3	0.58 ± 0.10	34 ± 1.9
	Chlorobenzenes		
	Rh: 1.89 $mg_{Rh}$$L^{-1}$	IS: 4-chlorotoluene		
	k_{obs} [h^{-1}]	k_{rel} [−]	$k_{rel,norm}$ [−]	$t_{1/2}$ [min]
chlorobenzene (CB)	3.0 ± 0.7	1.2 ± 0.2	1.00 ± 0.20	14 ± 3.4
1,2-diCB	3.2 ± 0.9	1.2 ± 0.4	0.98 ± 0.29	13 ± 3.8
1,3-diCB	3.1 ± 0.6	1.2 ± 0.2	0.99 ± 0.17	13 ± 2.5
1,4-diCB	2.4 ± 0.6	1.0 ± 0.2	0.80 ± 0.14	17 ± 4.6
1,2,3-triCB	2.3 ± 0.7	1.0 ± 0.5	0.77 ± 0.44	18 ± 5.0
1,2,4-triCB	1.8 ± 0.6	0.7 ± 0.3	0.58 ± 0.23	23 ± 8.0
1,3,5-triCB	1.2 ± 0.1	0.5 ± 0.1	0.41 ± 0.12	35 ± 1.8
1,2,3,4-tetraCB	2.2 ± 0.2	0.7 ± 0.1	0.60 ± 0.11	19 ± 1.5
1,2,3,5-tetraCB	2.7 ± 1.2	0.8 ± 0.2	0.68 ± 0.17	15 ± 7.2
1,2,4,5-tetraCB	1.9 ± 0.3	0.7 ± 0.1	0.54 ± 0.06	22 ± 3.1
pentaCB	1.0 ± 0.1	0.4 ± 0.2	0.35 ± 0.15	43 ± 6.5
hexaCB	0.1 ± 0.04	0.1 ± 0.04	0.07 ± 0.03	335 ± 110
	Mixed Halogenated Benzenes		
	Rh: 1.89 $mg_{Rh}$$L^{-1}$	IS: 4-chlorotoluene		
	k_{obs} [h^{-1}]	k_{rel} [−]	$k_{rel,norm}$ [−]	$t_{1/2}$ [min]
fluorobenzene	3.3 ± 0.5	0.8 ± 0.3		13 ± 1.9
chlorobenzene	4.7 ± 1.0	1.1 ± 0.3		8.8 ± 1.8
bromobenzene	5.0 ± 0.9	1.4 ± 0.3		8.4 ± 1.5
iodobenzene	3.1 ± 0.8	2.3 ± 0.4		14 ± 3.5
1-fluoro-4-chlorobenzene	3.7 ± 0.4	0.9 ± 0.2		11 ± 1.4
1-fluoro-4-bromobenzene	2.9 ± 0.6	1.1 ± 0.2		14 ± 2.9
1-chloro-4-bromobenzene	3.8 ± 1.5	1.2 ± 0.3		11 ± 4.4
1-chloro-4-iodobenzene	3.5 ± 0.7	2.4 ± 0.5		12 ± 2.3
benzene	1.9 ± 0.1	0.8 ± 0.1		22 ± 0.6

[a]All experiments were run in duplicate. Errors are composed of the errors of the pseudo-first-order kinetic fits and the standard deviation of the duplicate experiments. Rates for the substituted benzenes are given in the Supporting Information.

(LOD) and limits of quantification (LOQ) of all compounds are also reported in the Supporting Information.

Evaluation of Reaction Kinetics. Pseudo-first-order kinetics were observed for degradation of the halogenated benzenes and reactive standards. Hydrogen was assumed to be constant and available in excess. Pseudo-first-order rate constants (k_{obs}) were estimated using AQUASIM[36] by minimizing weighted least-squares estimates. Relative rate constants (k_{rel}) were obtained by normalizing to the rate constant of the reactive standard in the same batch experiment

$$k_{rel} = \frac{k_{obs,target}}{k_{obs,IS}}$$

Relative rate constants normalized to the rate constant of the respective monohalobenzene are reported as $k_{rel,norm}$.

Because degradation of the substances is surface-mediated, Langmuir−Hinshelwood kinetics were considered. At high starting material spike concentrations (500 μM) we did observe a change in the shape in the degradation curve, indicative of saturation kinetics. Nevertheless, we believe that with spike concentrations of 100 μM we are in the first-order regime of the Langmuir−Hinshelwood saturation curve. This was

supported by the fact that pseudo-first-order kinetics represented our data very well. Because the overall reaction kinetics in the first-order regime of a Langmuir−Hinshelwood system are an amalgam of the surface binding and substance transformation kinetics (see Supporting Information for more information on this point), the k_{obs} and k_{rel} values reported here reflect both the binding and the transformation.

■ RESULTS AND DISCUSSION

General Observations. The catalytic system with Rh/ Al$_2$O$_3$ and H$_2$ was found to be capable of efficiently degrading a wide range of halogenated benzenes under mild conditions (ambient temperature, 1 atm H$_2$, 1.89 mg$_{Rh}$ L^{-1} in the form of 5% Rh/Al$_2$O$_3$ catalyst). Assuming that every Rh atom on the surface corresponds to an active site, an absolute maximum of approximately 8 μM active sites was estimated. The scope of the catalysts includes complete dehalogenation of all poly- fluorobenzenes, all polychlorobenzenes, bromobenzene, iodo- benzene, and selected mixed halogenated benzenes and hydrogenation of benzene and selected unhalogenated benzene derivatives. The pseudo-first-order rate constants (k_{obs}), rate constant normalized to the reactive standard (k_{rel}), and half- lives ($t_{1/2}$, based on k_{obs}) of all tested substances are reported in Table 1. Details about the reactive standard normalization and the rate variability are given in the Supporting Information.

Fluorinated Benzenes. All fluorobenzene (FB) congeners underwent rapid degradation when they were subjected to batch reaction conditions. Degradation reactions with the congeners were either equal to or slower than fluorobenzene ($t_{1/2} \approx 11$ min) with half-lives between 11 and 42 min (Table 1). During the loss of FB congeners, lower fluorinated congeners and occasionally cyclohexene were observed as minor intermediates. Benzene was formed as the major intermediate, and cyclohexane was the final stable organic product of the catalytic reactions. Fluoride concentrations were not determined in the experiments, but based on our previous study,[10] we believe that F$^-$ release is stoichiometric. In Figure 1, degradation of hexafluorobenzene and formation of intermedi- ates is shown as an illustrative example for all fluorinated benzenes.

Proposed Mechanistic Pathway. Results from experiments with the FB congeners are in agreement with our previous observations for fluorobenzene, suggesting that the mechanistic hypothesis proposed for degradation of fluorobenzene with Rh/Al$_2$O$_3$ and H$_2$[10] can be applied to higher fluorinated benzenes. Benzene is an important intermediate and cyclo- hexane the end product of all catalytic reactions. No fluorinated cyclohexadienes, cyclohexenes, or cyclohexanes were observed during the course of the reactions. From experiments with fluorobenzene, Rh/Al$_2$O$_3$, and deuterated reaction components, we know that benzene hydrogenation is reversible, defluorina- tion is irreversible, and saturated substances are not reactive in the catalytic system.[10] The proposed mechanistic pathway therefore involves initial irreversible defluorination steps forming benzene, followed by reversible hydrogenation of benzene to cyclohexadiene and cyclohexene, and finally irreversible hydrogenation of cyclohexene to cyclohexane. A kinetic model showed that adsorption and desorption of all reaction components to and from the catalyst surface significantly influenced the reaction kinetics.[10] The same kinetic model is also applicable to the polyfluorinated benzenes. In the model (Figure 3c), the intermediate, I, represents the sum of (possibly surface-bound) unknown intermediates,
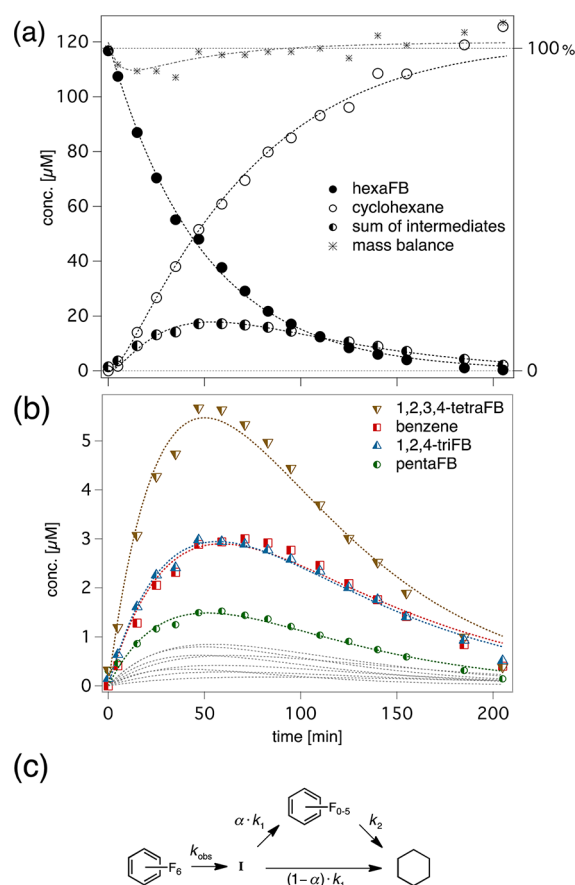

Figure 1. (a) Hexafluorobenzene degradation and cyclohexane formation: half-filled dots represent the sum of all intermediates; traces were fit to the model shown in Figure 1c. (b) Detail of intermediate growth and decay traces during degradation of hexafluorobenzene, fit to a growth and decay model shown in Figure SI-2b, Supporting Information. Traces showing individual data points for fluorobenzene, difluorobenzenes, 1,2,3-triFB, 1,3,5-triFB, 1,2,4,5- tetraFB, and 1,2,4,5-tetraFB are also given in the Supporting Information. (c) Kinetic model for degradation of hexafluorobenzene to cyclohexane through the sum of all intermediates. Arrows correspond to pseudo-first-order degradation. I represents an unknown intermediate, and α is the fraction of the reaction proceeding through the intermediate benzene. Differential equations representing the model are given in the Supporting Information.

whose nature is discussed below. For hexafluorobenzene, the adapted version of the model is shown in Figure 1c, the model fits in Figure 1a. The differential equation system representing the model is given in the Supporting Information.

Differences in Rate Constants of the FB Congeners. The FB congeners are thought to react by the same general mechanism as fluorobenzene. However, differences in the degradation rates (Table 1) between the various congeners show that the substituents influence the reaction. Analysis of the degradation rate constants of the set of FB congeners revealed two major trends.

(1) Degradation rate constants decrease with increasing number of fluorine substituents (Figure 2a).

(2) Degradation rate constants increase with increasing number of bonds with two adjacent fluorine substituents (Figure 2b).

Both trends can be observed from plotting the $k_{rel,norm}$ values of the FB congeners versus the number of bonds with adjacent

a) Number of **F** substituents

(1) (2) (3)

b) Number of **bonds with adjacent F** substituents
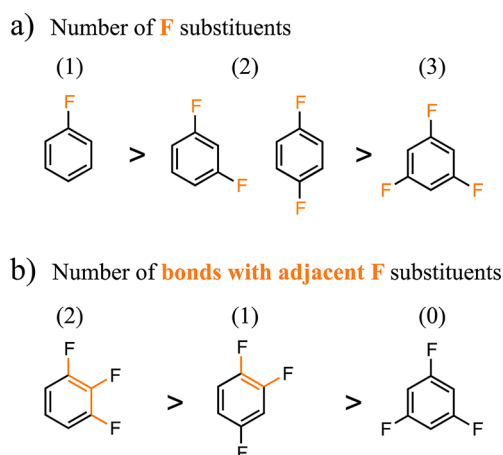
(2) (1) (0)

Figure 2. Two examples to illustrate the trends observed within the degradation rate constants of the FB congeners: (a) faster degradation with decreasing number of fluorine substituents (number given in parentheses) and (b) faster degradation with increasing number of bonds with two adjacent fluorine substituents (number given in parentheses).

fluorine substituents of the molecule (Figure 3). Neither of the trends is easily observable in the plot without congener
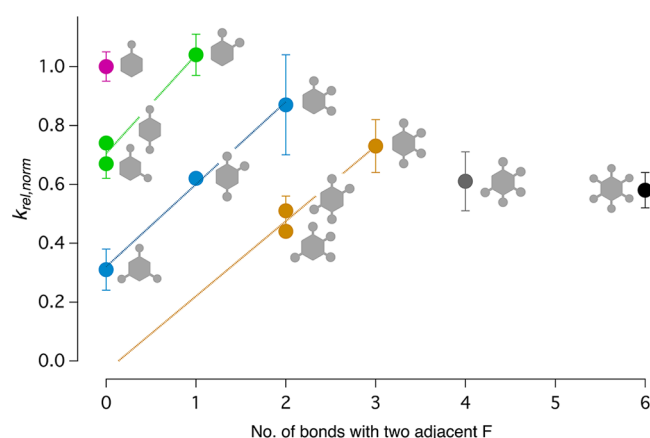

Figure 3. Normalized degradation rate constants of all FB congeners plotted against their number of bonds with two adjacent fluorine substituents. Lines are the linear fits through the di-, tri-, and tetrafluorobenzene rate constants and indicate the trends of increasing degradation rate with increasing number of bonds with adjacent fluorine substituents. Linear fits are $y = 0.71 + 0.34 (R^2 = 0.97)$ for the difluorobenzenes, $y = 0.32 + 0.28 (R^2 = 0.99)$ for the trifluorobenzenes, and $y = 0.04 + 0.26 (R^2 = 0.95)$ for the tetrafluorobenzenes.

classification, as they interfere with each other. However, the trends become clear if the congeners are grouped appropriately.

The trend showing slower degradation with increasing fluorine substitution is illustrated in Figure 2a and applies within groups of FB congeners with the same number of bonds with two adjacent fluorine substituents. For example, FB degrades faster than 1,3-diFB or 1,4-diFB, which degrade faster than 1,3,5-triFB. In this series, none of the congeners have adjacent fluorine substituents. A similar trend in the rates is observed in the group with one or two bonds with two adjacent fluorine substituents (Figure 3).

Degradation rate constants tended to increase in molecules with increasing numbers of bonds with two adjacent fluorine substituents. This trend applies to the groups with the same

number of fluorine substituents (Figure 3), namely, for the difluorobenzenes, trifluorobenzenes (Figure 2b), and tetrafluorobenzenes. In these groups faster degradation rate constants were observed for congeners with more bonds with adjacent fluorine substituents. For example, in the series with trifluorobenzenes, 1,2,3-triFB degraded faster than 1,2,4-triFB, which degraded faster than 1,3,5-triFB.

Intermediate Formation. Formation of intermediates during the catalytic reaction of the FB congeners was analyzed to gain more information about the pathways involved in degradation. In general, almost all possible lower fluorinated FB congeners were observed when a higher FB congener was degraded. Nevertheless, some degradation pathways were clearly dominant. In order to identify the main degradation pathways quantitatively, the initial formation rate was derived for each observed intermediate in each experiment by fitting the initial phase of the reaction (three to five data points) by linear regression.

The two most prevalent fluorinated intermediates formed from each FB congener were used for mechanistic interpretation. The following trends were observed.

(1) For all the FB congeners with adjacent fluorine substituents, the first two intermediates observed were formed through removal of either one or both of the adjacent fluorine substituents.

(2) The fluorine substituents with the most adjacent fluorine substituents were preferentially removed (e.g., 1,3-diFB produced from 1,2,3-triFB and 1,2,4-triFB from 1,2,3,4-tetraFB).

(3) In the cases where a single fluorine substituent and two or more adjacent fluorine substituents were present in the same molecule, the intermediates where the single fluorine substituent was removed were either not observed (e.g., 1,2-diFB was not observed from 1,2,4-triFB) or formed in amounts more than 10 times lower than the two most important intermediates (e.g., 1,2,3-triFB was a very minor product from 1,2,3,5-tetraFB).

Often benzene was among the fastest forming intermediates, showing that the catalyst was capable of removing all fluorine substituents without releasing fluorinated intermediates from the catalyst surface to the bulk phase. This observation is consistent with the proposed reaction mechanism where a portion of the reacting species remains sorbed on the surface during either a part or all of the catalytic reaction.[10]

Binding of the FB Congeners to the Catalyst. We hypothesize that the binding of FB congeners onto Rh/Al_2O_3 is a very important step in the degradation reactions, influencing both the observed degradation rates and the types of intermediates observed. In fact, it appears that the faster degradation with increasing adjacent fluorine substituents and the observed preference of the catalyst for removing fluorine atoms from bonds with adjacent fluorine substituents were a result of both the thermodynamics and the kinetics of the adsorption of the FB congeners onto Rh/Al_2O_3.

Analyzing and modeling the mass balances of the FB congeners degradation reactions showed that the binding to the catalyst must have played an important role in the surface-mediated degradation reaction. Carbon mass balances dropped to approximately 80% (range 70−95%) compared to the initially spiked concentrations (24 experiments) during the first third of the experiments but recovered to approximately 100% (range 77−122%) at the end of the reactions. The model

shown in Figure 1c captures the drop in the mass balance for hexafluorobenzene (Figure 1a) during the first 50 min very well. The model includes an unknown intermediate (I), which is not observed in the batch experiments and is therefore responsible for the mass balance drop in the modeling. We speculate that the unknown and unobserved intermediate (I) represents all surface-bound species during the degradation reactions. We do not know what the nature of the sorbed species was; I summarizes all physisorbed and/or chemisorbed intermediates on the surface. Also, kinetic modeling of fluorobenzene degradation indicated that about 22% of the initially spiked compound stayed surface bound until the end product of the reaction was released to the bulk phase.[10] In the H$_2$-free control, this clear drop in mass balance was not observed, and we speculate that the Rh surface needs to be activated by H$_2$ to sorb the fluorobenzene substrates.

The observed trends in degradation rates of the FB congeners and the trends for intermediate formation could be combined in one model based on substrate binding. The model would need two rules: First, stronger binding leads to faster degradation and, second, substituents that are closest to the binding site are removed first. Ryzhov et al. modeled the gas-phase binding of all FB congeners to a Cr$^+$ ion and found decreasing binding energies with increasing number of fluorine substituents.[37] Furthermore, their calculations indicated that an in-plane binding with two adjacent fluorine substituents was favored over π-facial binding whenever there is a bond with two adjacent fluorine substituents. While the Ryzhov et al. and our system have substantial differences, it is interesting to note that they also observe a different pattern of interaction for the ortho-F$_2$-containing compounds. The trends they observed for binding energy are consistent with the trends we observed for degradation rates in this study; higher binding energies correlate with increased degradation rate due to (1) decreased binding energies with increasing number of fluorine substituents and (2) higher binding energies when bonds with adjacent fluorine substituents are present. Binding of Rh/Al$_2$O$_3$ to the adjacent fluorine substituents could also explain the intermediate pattern observed if the catalyst was bound to the adjacent fluorine substituents and was capable of removing one or both of them. Nevertheless, further investigation is necessary to establish the relationship between binding energy and degradation rate of fluorobenzenes in the specific case of rhodium or Rh/Al$_2$O$_3$ in aqueous solution.

Chlorinated Benzenes. The chlorobenzene (CB) congeners were tested as a comparison to the degradation of the FB congeners to examine whether they followed the same mechanistic principles.

All chlorobenzene (CB) congeners degraded rapidly when subjected to the reaction conditions, with half-life times similar to those of the corresponding FB congeners. An exception was the sterically most hindered hexachlorobenzene, which degraded 10 times slower than hexafluorobenzene ($t_{1/2} \approx 335$ min). Analogous to the FB congeners, the chlorobenzenes fully degraded to form cyclohexane, benzene was the main intermediate, and lower chlorinated congeners were minor intermediates.

Degradation Trends and Intermediates. A general trend of decreasing rates with increasing number of chlorine substituents was observed for the group of the CB congeners. Similarly, decreasing rates with increasing chlorine substitution were observed using a palladium-based catalyst in the aqueous phase,[38] and with Ni/SiO$_2$ in the gas phase,[39] the trend is

generally attributed to steric constraints. Within the groups of congeners with two and four chlorine substituents, only small differences in the degradation rates were observed. For the triCBs, 1,2,3-triCB was degraded faster than 1,2,4-triCB, which was degraded faster than 1,3,5-triCB. The same trend for triCB degradation was observed by Keane et al.[39] in the gas phase. This is also the same trend that was observed for the FB congeners (Figure 2b). However, the trends for the di- and tetrachlorobenzenes were not consistent with those for the di- and tetrafluorobenzenes, and therefore, we reason that the CB congener degradation was governed by factors different from those we proposed for the FB congeners.

Analysis of the initial formation rates for the chlorinated intermediates indicated that, once the congener is adsorbed, removal of chlorine substituents was governed by steric factors. In all cases, the first chlorine substituent removed was the least sterically hindered (e.g., the 5-substituent was removed first from 1,2,3,5-tetraCB and the 4-substituent from 1,2,4-triCB). Chlorine substituents without at least one hydrogen-atom substituent adjacent were not removed, with only one exception where 1,2,4-triCB was observed as an intermediate of 1,2,3,4-tetraCB. However, the major product of 1,2,3,4-tetraCB was 1,2,3-triCB. It is not known why more open sites reacted faster, but we speculate that attack of the carbon by either Rh or Rh−H is slowed by steric crowding by neighboring chlorine atoms.

Comparison of FB and CB Congener Degradation. The degradation pathway pattern of the CB congeners with removal of the sterically most accessible chlorine substituent (highest number of adjacent hydrogen substituents) stands in contrast to the FB congeners, where in all cases the most "crowded" fluorine substituent (lowest number of adjacent hydrogen substituents) was removed first. In Figure 4, the difference in the degradation pathways is illustrated with the example of the 1,2,3,5-tetrahalobenzenes. The main halogenated intermediate formed during 1,2,3,5-tetraFB degradation was 1,3,5-triFB, which was not formed during the corresponding tetraCB
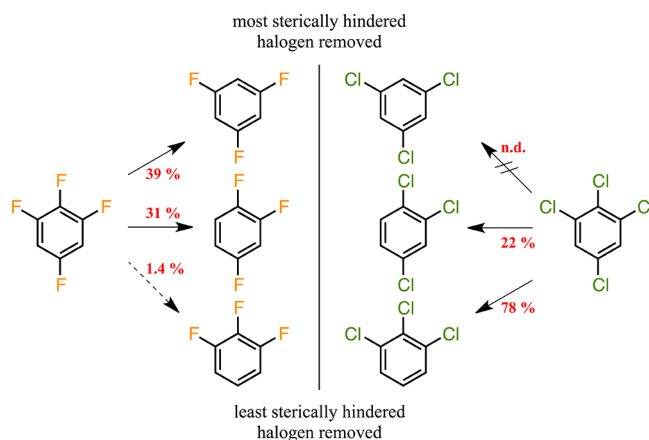

Figure 4. Comparison of the intermediate pattern observed during degradation of 1,2,3,5-tetraFB and 1,2,3,5-tetraCB. Numbers by the arrows indicate the percentage of all halogenated intermediates that is represented by the shown intermediate. The sterically most hindered halogen is preferably removed from the fluorobenzenes, whereas the sterically least hindered halogen is preferably removed from the chlorobenzenes. Intermediates observed during fluoro- and chlorobenzene degradation clearly show opposite trends for the degradation pathway.

degradation. On the other hand, the main intermediate formed from 1,2,3,5-tetraCB was 1,2,3-triCB; the analogous intermediate during tetraFB degradation was very minor. The 1,2,4-trihalobenzene was formed during degradation of both the 1,2,3,5-tetraCB and the 1,2,3,5-tetraFB. The different degradation patterns of the polyfluoro- and polychlorobenzenes suggest that the two classes of compounds are degraded following different mechanistic principles, although the reactions yield the same final end product.

The degradation rate constants for both congener groups were analyzed in a semiquantitative way in order to compare them. For both of the groups of congeners a decreasing rate constant was observed with increasing halogen substitution. Using eq 1, a least-squares regression analysis was performed using the sets of degradation rates constants ($k_{rel,norm}$) of either the CB or the FB congeners to obtain x using Excel solver. The coefficient X refers to the number of halogen substituents.

$$k_{rel,norm} = 1 + x \cdot (X - 1) \tag{1}$$

For the CB congeners, the best fit was −0.16 for the variable x ($R^2 = 0.81$). Degradation rate constants decreased on average by 16% for every extra chlorine substituent; 81% of the variability in the data could be explained by the number of chlorine substituents. For the FB congeners the fit was worse ($x = -0.13$, $R^2 = 0.58$), indicating that another variable is needed to explain the FB congener degradation data. An equation that includes the number of bonds with two adjacent fluorine substituents was chosen (eq 2). The variables f and a describe the fractional contribution of the number of fluorine atoms (F) and the number of adjacent fluorine substituents (A), respectively.

$$k_{rel,norm} = 1 + f \cdot (F - 1) + a \cdot A \tag{2}$$

The least-squares regression analysis using Excel solver showed that the best fits for the variables were −0.31 and +0.20 for f and a, respectively ($R^2 = 0.94$). The degradation rate constants are on average decreased by 31% for every extra fluorine substituent and increased by 20% for every bond with adjacent fluorine substituents. The high R^2 indicates that eq 2 reasonably models the FB congeners data and that both variables are needed to capture the variability in the data. All model fits are shown graphically in the Supporting Information.

Preferential Removal of Halogens. To establish a catalytic order of preference of the Rh/Al$_2$O$_3$ catalyst for the halogen−carbon bonds, degradation rates were determined for bromobenzene and iodobenzene in addition to fluoro- and chlorobenzene. They all degraded rapidly with Rh/Al$_2$O$_3$ and H$_2$. Differences in the degradation rate constants of the four monohalobenzenes were small; half-lives ranged from 8.4 to 14 min (Table 1). Comparison of k_{rel} indicates that fluorobenzene degraded the slowest, followed by chlorobenzene and bromobenzene, and iodobenzene degraded significantly faster than the other monohalobenzenes.

To further test the preferences of the catalyst, benzenes containing two different halogen substituents were subjected to the reaction conditions. The four tested mixed dihalobenzenes degraded at rates similar to the monosubstituted benzenes, and comparing k_{rel}, the iodine-containing benzene degraded significantly faster than the others (Table 1). The identity of the observed intermediates showed which of the halogens was removed preferentially. During degradation of mixed 1,4-dihalobenzenes (fluoro/chloro, chloro/bromo, fluoro/bromo,

chloro/iodo), it was clear from the intermediates that were formed that one of the halogens was preferentially removed. In each case, the first halogen removed was the one with the weaker C−X bond, consistent with an overall catalyst tendency to remove a halogen in intramolecular competition with the following selectivity: F < Cl < Br < I. This trend is interesting, especially given that the rates of the monohalobenzenes were very similar to each other, leading to the expectation of similar rates of removal for the mixed dihalobenzenes. Figure 5
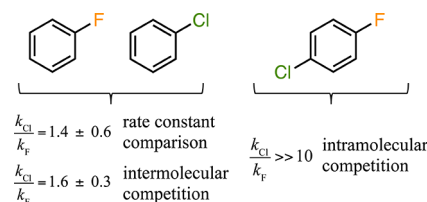
Figure 5. Comparison of intermolecular and intramolecular competition of dechlorination and defluorination. Rate constant comparison is the ratio of the pseudo-first-order rate constants of CB and FB derived from two individual batch experiments, and the intermolecular competition is the ratio of the rate constants when FB and CB were spiked into the same batch experiment. For intramolecular competition, initial rates of formation of CB and FB from 1-chloro-4-fluorobenzene were compared.

illustrates this dramatic difference in intra- versus intermolecular halogen selectivity. We ascribe the seemingly paradoxical observations to adsorption being the main driver. If sorption is the rate-determining step (i.e., $k_2 \gg k_{-1}$ in eq SI-9, Supporting Information) and chloro- and fluorobenzene have similar sorption on and off rates, then it follows that similar degradation rates would be observed for these two substrates. The observation that the C−Cl bond is cleaved more rapidly than the C−F bond in 1-chloro-4-fluorobenzene is consistent with this model and would indicate that, once the halobenzene is bound, the C−Cl bond is more readily cleaved than the C−F bond.

Selective Inhibition of Hydrogenation. A notable observation was made in the batch experiments with iodobenzene and 1-chloro-4-iodobenzene: degradation rates of the reactive standard (4-chlorotoluene) and hydrogenation of the intermediate benzene were clearly reduced relative to our other experiments. This effect also resulted in relatively high k_{rel} (see Table 1) for the iodine-containing benzenes, although the rate constants did not significantly differ from the other halogenated benzenes. Additional tests were conducted to study the effect of organoiodine or iodide (I$^-$), respectively. Chlorobenzene degradation without additive was compared to chlorobenzene degradation with addition of 100 μM NaI and to degradation of 1-chloro-4-iodobenzene. In fact, *dechlorination* rates were reduced by about a factor of 2 when 100 μM iodide was present, and this inhibition was the same whether the I$^-$ was added as a salt or freshly removed from 1-chloro-4-iodobenzene. The *hydrogenation* rate was reduced even more (up to 10 times slower) in the presence of I$^-$. Inhibitory effects of iodide were previously shown for Pd-based dehalogenation catalysts and attributed to its strong affinity for metallic surfaces.[40,41] Alternatively, the slowing down of the reaction in the presence of iodide could be caused by scavenging of a key intermediate, such as surface-bound H atoms. If iodide binding to the surface is the inhibition mechanism, the stronger inhibition of the hydrogenation reaction relative to the

dehalogenation reaction by I⁻ indicates that the two reaction types are not directly coupled in the mechanism and may be occurring at different sites. We speculate that the two different reaction types are actually catalyzed by two different active sites on the heterogeneous Rh/Al$_2$O$_3$ surface.

Wide Halogen Scope. In this work, it was demonstrated that the catalytic system of Rh/Al$_2$O$_3$ and H$_2$ in water can be widely applied for dehalogenation and hydrogenation of benzenes. Most interestingly, the catalyst has a special affinity for fluorine removal. Hydrodefluorination rates are not significantly different from other hydrodehalogenation rates. Perhaps surprisingly, hexafluorobenzene is degraded more than 10 times faster than hexachlorobenzene. We note though that our catalyst is rather slow at degrading chlorinated substances in water compared to previously reported catalysts.[41,42] The ambient reaction temperature and low pressure of H$_2$ make this method potentially viable for remediation of groundwater contaminated with halogenated benzenes, including fluorobenzenes. It should be noted that the catalyst is ineffective for reduction of saturated fluorocarbon, which are also an important class of pollutants.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Method details, Langmuir−Hinshelwood calculations, reactive standard normalization and rate variability details, hexafluorobenzene intermediate traces and models for fitting, graphics for model fits for FB and CB congener degradation rate constants, limits of detection and quantification, and structures illustrating reaction scope. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: kris.mcneill@env.ethz.ch.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Braun, T.; Wehmeier, F. C−F Bond Activation of Highly Fluorinated Molecules at Rhodium: From Model Reactions to Catalysis. *Eur. J. Inorg. Chem.* **2011**, *5*, 613.

(2) Grushin, V. V.; Alper, H. Transformations of Chloroarenes, Catalyzed by Transition-Metal Complexes. *Chem. Rev.* **1994**, *94*, 1047.

(3) Keane, M. Supported Transition Metal Catalysts for Hydrodechlorination Reactions. *ChemCatChem* **2011**, *3*, 800.

(4) Bryant, R. Pharmaceutical Fine Chemicals Global Perspectives 2000. *Informa Chemicals Industry Report*, Informa Chemicals: Kent, U.K., 2000.

(5) Key, B. D.; Howell, R. D.; Criddle, C. S. Fluorinated organics in the biosphere. *Environ. Sci. Technol.* **1997**, *31*, 2445.

(6) O'Hagan, D. Fluorine in health care: Organofluorine containing blockbuster drugs. *J. Fluorine Chem.* **2010**, *131*, 1071.

(7) Boyd, E. M.; Killham, K.; Wright, J.; Rumford, S.; Hetheridge, M.; Cumming, R.; Meharg, A. A. Toxicity assessment of xenobiotic contaminated groundwater using lux modified Pseudomonas fluorescens. *Chemosphere* **1997**, *35*, 1967.

(8) Schultz, M. M.; Furlong, E. T. Trace Analysis of Antidepressant Pharmaceuticals and Their Select Degradates in Aquatic Matrixes by LC/ESI/MS/MS. *Anal. Chem.* **2008**, *80*, 1756.

(9) Metcalfe, C.; Miao, X.; Koenig, B.; Struger, J. Distribution of acidic and neutral drugs in surface waters near sewage treatment plants in the lower Great Lakes, Canada. *Environ. Toxicol. Chem.* **2003**, *22*, 2881.

(10) Baumgartner, R.; McNeill, K. Hydrodefluorination and Hydrogenation of Fluorobenzene under Mild Aqueous Conditions. *Environ. Sci. Technol.* **2012**, *46*, 10199.

(11) Aizenberg, M.; Milstein, D. Catalytic activation of carbon-fluorine bonds by a soluble transition metal complex. *Science* **1994**, *265*, 359.

(12) Blum, J.; Rosenfeld, A.; Gelman, F.; Schumann, H.; Avnir, D. Hydrogenation and dehalogenation of aryl chlorides and fluorides by the sol-gel entrapped RhCl$_3$-Aliquat 336 ion pair catalyst. *J. Mol. Catal. A: Chem.* **1999**, *146*, 117.

(13) Buil, M. L.; Esteruelas, M. A.; Niembro, S.; Oliván, M.; Orzechowski, L.; Pelayo, C.; Vallribera, A. Dehalogenation and hydrogenation of aromatic compounds catalyzed by nanoparticles generated from rhodium bis(imino)pyridine complexes. *Organometallics* **2010**, *29*, 4375.

(14) Stanger, K. J.; Angelici, R. J. Hydrodefluorination of fluorobenzene catalyzed by rhodium metal prepared from [Rh-(COD)$_2$]⁺BF4⁻ and supported on SiO$_2$ and Pd-SiO$_2$. *J. Mol. Catal. A: Chem* **2004**, *207*, 59.

(15) Young, R. J.; Grushin, V. V. Catalytic C-F bond activation of nonactivated monofluoroarenes. *Organometallics* **1999**, *18*, 294.

(16) Adonin, N. Y.; Starichenko, V. F. Hydrogenolysis of C-F bonds in fluorinated aromatic hydrocarbons catalysed by nickel complexes. *Mendeleev Commun.* **2000** 60.

(17) Desmarets, C.; Kuhl, S.; Schneider, R.; Fort, Y. Nickel(0)/imidazolium chloride catalyzed reduction of aryl halides. *Organometallics* **2002**, *21*, 1554.

(18) Fischer, P.; G√∂tz, K.; Eichhorn, A.; Radius, U. Decisive Steps of the Hydrodefluorination of Fluoroaromatics using [Ni(NHC)2]. *Organometallics* **2012**, *31*, 1374.

(19) Wu, J.; Cao, S. Nickel-Catalyzed Hydrodefluorination of Fluoroarenes and Trifluorotoluenes with Superhydride (Lithium Triethylborohydride). *ChemCatChem* **2011**, *3*, 1582.

(20) Zhao, W.; Wu, J.; Cao, S. Highly Efficient Nickel(II) Chloride/Bis(tricyclohexylphosphine)nickel(II) Chloride-Cocatalyzed Hydrodefluorination of Fluoroarenes and Trifluorotoluenes with Superhydride. *Adv. Synth. Catal.* **2012**, *354*, 574.

(21) Cellier, P. P.; Spindler, J. F.; Taillefer, M.; Cristau, H. J. Pd/C-catalyzed room-temperature hydrodehalogenation of aryl halides with hydrazine hydrochloride. *Tetrahedron Lett.* **2003**, *44*, 7191.

(22) Sawama, Y.; Yabe, Y.; Shigetsura, M.; Yamada, T.; Nagata, S.; Fujiwara, Y.; Maegawa, T.; Monguchi, Y.; Sajiki, H. Platinum on Carbon-Catalyzed Hydrodefluorination of Fluoroarenes using Isopropyl Alcohol-Water-Sodium Carbonate Combination. *Adv. Synth. Catal.* **2012**, *354*, 777.

(23) Vela, J.; Smith, J. M.; Yu, Y.; Ketterer, N. A.; Flaschenriem, C. J.; Lachicotte, R. J.; Holland, P. L. Synthesis and reactivity of low-coordinate iron(II) fluoride complexes and their use in the catalytic hydrodefluorination of fluorocarbons. *J. Am. Chem. Soc.* **2005**, *127*, 7857.

(24) Reade, S. P.; Mahon, M. F.; Whittlesey, M. K. Catalytic Hydrodefluorination of Aromatic Fluorocarbons by Ruthenium N-Heterocyclic Carbene Complexes. *J. Am. Chem. Soc.* **2009**, *131*, 1847.

(25) Zhan, J.-H.; Lv, H.; Yu, Y.; Zhang, J.-L. Catalytic C-F Bond Activation of Perfluoroarenes by Tricoordinated Gold(I) Complexes. *Adv. Synth. Catal.* **2012**, *354*, 1529.

(26) Yang, H.; Gao, H. R.; Angelici, R. J. Hydrodefluorination of fluorobenzene and 1,2-difluorobenzene under mild conditions over rhodium pyridylphosphine and bipyridyl complexes tethered on a silica-supported palladium catalyst. *Organometallics* **1999**, *18*, 2285.

(27) Aramendia, M. A.; Borau, V.; Carcia, I. M.; Jimenez, C.; Marinas, A.; Marinas, J. M.; Urbano, F. J. Hydrogenolysis of aryl halides by hydrogen gas and hydrogen transfer over palladium-supported catalysts. *C.R. Acad. Sci. II B* **2000**, *3*, 465.

(28) Klahn, M.; Fischer, C.; Spannenberg, A.; Rosenthal, U.; Krossing, I. Hydrodefluorination of non-activated C-F bonds by diisobutyl-aluminiumhydride via the aluminium cation [i-Bu$_2$Al]$^+$. *Tetrahedron Lett.* **2007**, *48*, 8900.

(29) Ukisu, Y.; Miyadera, T. Hydrogen-transfer hydrodehalogenation of aromatic halides with alcohols in the presence of noble metal catalysts. *J. Mol. Catal. A: Chem.* **1997**, *125*, 135.

(30) Carvalho, M. F.; Ferreira, M. I. M.; Moreira, I. S.; Castro, P. M. L.; Janssen, D. B. Degradation of fluorobenzene by *Rhizobiales* strain F11 via ortho cleavage of 4-fluorocatechol and catechol. *Appl. Environ. Microbiol.* **2006**, *72*, 7413.

(31) Li, H.; Liu, Y. H.; Luo, N.; Zhang, X. Y.; Luan, T. G.; Hu, J. M.; Wang, Z. Y.; Wu, P. C.; Chen, M. J.; Lu, J. Q. Biodegradation of benzene and its derivatives by a psychrotolerant and moderately haloalkaliphilic *Planococcus* sp. strain ZD22. *Res. Microbiol.* **2006**, *157*, 629.

(32) Murphy, C. D. Biodegradation and biotransformation of organofluorine compounds. *Biotechnol. Lett.* **2010**, *32*, 351.

(33) Strunk, N.; Engesser, K.-H. Degradation of fluorobenzene and its central metabolites 3-fluorocatechol and 2-fluoromuconate by Burkholderia fungorum FLU100. *Appl. Microbiol. Biotechnol..* **2012** 1.

(34) Moreira, I.; Amorim, C.; Carvalho, M.; Castro, P. L. Degradation of difluorobenzenes by the wild strain *Labrys portucalensis. Biodegradation* **2012**, *23*, 653.

(35) Hornstein, B. J.; Aiken, J. D.; Finke, R. G. Nanoclusters in Catalysis: A Comparison of CS$_2$ Catalyst Poisoning of Polyoxoanion- and Tetrabutylammonium-Stabilized 40 ± 6 Å Rh(0) Nanoclusters to 5 Rh/Al$_2$O$_3$, Including an Analysis of the Literature Related to the CS$_2$ to Metal Stoichiometry Issue. *Inorg. Chem.* **2002**, *41*, 1625.

(36) Reichert, P. *Concepts underlying a computer program for the identification and simulation of aquatic systems, CH-8600*; Dübendorf, Switzerland, 1994.

(37) Ryzhov, V.; Yang, C.-N.; Klippenstein, S. J.; Dunbar, R. C. Binding energies of chromium cations with fluorobenzenes from radiative association kinetics. *Int. J. Mass Spectrom.* **1999**, *185/186/187*, 913.

(38) Zhu, B.-W.; Lim, T.-T. Catalytic Reduction of Chlorobenzenes with Pd/Fe Nanoparticles: Reactive Sites, Catalyst Stability, Particle Aging, and Regeneration. *Environ. Sci. Technol.* **2007**, *41*, 7523.

(39) Keane, M. A.; Pina, G.; Tavoularis, G. The catalytic hydrodechlorination of mono-, di- and trichlorobenzenes over supported nickel. *Appl. Catal., B* **2004**, *48*, 275.

(40) Knitt, L. E.; Shapley, J. R.; Strathmann, T. J. Rapid metal-catalyzed hydrodehalogenation of iodinated X-ray contrast media. *Environ. Sci. Technol.* **2008**, *42*, 577.

(41) Mackenzie, K.; Frenzel, H.; Kopinke, F. D. Hydrodehalogenation of halogenated hydrocarbons in water with Pd catalysts: Reaction rates and surface competition. *Appl. Catal., B* **2006**, *63*, 161.

(42) Kopinke, F.-D.; Angeles-Wedler, D.; Fritsch, D.; Mackenzie, K. Pd-catalyzed hydrodechlorination of chlorinated aromatics in contaminated waters: Effects of surfactants, organic matter and catalyst protection by silicone coating. *Appl. Catal. B, Environ.* **2010**, *96*, 323.