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Phosphinorhodium-Catalyzed Dehalogenation of Chlorinated and Fluorinated Ethylenes: Distinct Mechanisms with Triethylsilane and Dihydrogen

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Catalytic dehalogenation of chlorinated and fluorinated ethylenes by (PR₃)₃RhCl complexes is described. The C–Cl and C–F bonds are activated by the catalyst in the presence of triethylsilane (Et₃SiH) or dihydrogen (H₂). Spectroscopic studies, in addition to substrate preference, indicate that rhodium hydride species are important intermediates. Kinetic parameters and product distribution for dehalogenation reactions were determined using NMR spectroscopy. Evidence for sequential chlorine removal was obtained, and the rates of dehalogenation were found to increase with decreasing halogen content. It was also shown that this catalytic system has a preference for sp²-over sp³-hybridized carbon–halogen bonds. Dechlorination using (PPh₃)₃RhCl and either H₂ or Et₃SiH supports an insertion/β-chloride elimination mechanism; however, the two systems display distinct differences. On the basis of these differences, the dominant pathway for Et₃SiH is proposed to involve rhodium(I), while the H₂ system is proposed to primarily involve rhodium(III). This is supported with isotopic labeling studies using D₂, Et₃SiD, and (PPh₃)₃RhD, which yield different stereochemistry of dechlorinated products. With D₂, only products consistent with *syn*-β-chloride elimination were observed, while with Et₃SiD and (PPh₃)₃RhD both *syn*- and *anti*-β-chloride elimination products were observed. In addition, NMR spectroscopic evidence of different hydride intermediates in the H₂ and Et₃SiH systems was obtained. Different pathways for dehalogenation with Et₃SiH and H₂ is further supported by the observation of 1,2-addition (hydrogenation) products using H₂ and the lack of 1,2-addition (hydrosilylation) products using Et₃SiH.

Introduction

Thousands of tons of persistent chlorocarbons are produced annually, many of which are toxic and bioaccumulative.^{1–3} Chlorinated ethylenes, specifically perchloroethylene (PCE) and trichloroethylene (TCE), are potential carcinogens that are found in both soil and water systems.^{1–8} The toxic effects associated with these complexes are related to the chlorine substituents. Accordingly, removal of the chlorine atoms leads to detoxification.⁹ For instance, vinyl chloride, a known carcinogen, yields nontoxic ethylene upon dechlorination.¹⁰

Remediation of these pollutants by dechlorination has involved the use of zerovalent metals,^{11–19} electrochemical processes,^{20–25} and microbial degradation.^{5,7,26–28} Several heterogeneous noble metals have also been shown to degrade

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(1) Moran, M. J.; Zogorski, J. S.; Squillace, P. J. *Environ. Sci. Technol.* **2007**, *41*, 74–81.
(2) Doherty, R. E. *Environ. Forensics* **2000**, *1*, 83–93.
(3) Doherty, R. E. *Environ. Forensics* **2000**, *1*, 69–81.
(4) Glod, G.; Angst, W.; Holliger, C.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1997**, *31*, 253–260.
(5) Glod, G.; Brodmann, U.; Angst, W.; Holliger, C.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1997**, *31*, 3154–3160.
(6) Squillace, P. J.; Moran, M. J.; Lapham, W. W.; Price, C. V.; Clawges, R. M.; Zogorski, J. S. *Environ. Sci. Technol.* **1999**, *33*, 4176–4187.
(7) Gantzer, C. J.; Wackett, L. P. *Environ. Sci. Technol.* **1991**, *25*, 715–722.
(8) Leisinger, T. B., W. *Poorly Degradable Substances*; VCH Verlagsgesellschaft: Weinheim, 1986; Vol. 8, pp 475–513.
(9) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2002**, *102*, 4009–4091.
(10) Clewell, H. J.; Gentry, P. R.; Gearhart, J. M.; Allen, B. C.; Andersen, M. E. *Sci. Total Environ.* **2001**, *274*, 37–66.

(11) Song, H.; Carraway, E. R. *Appl. Catal., B* **2008**, *78*, 53–60.
(12) Dries, J.; Bastiaens, L.; Springael, D.; Agathos, S. N.; Diels, L. *Environ. Sci. Technol.* **2004**, *38*, 2879–2884.
(13) Dayan, H.; Abrajano, T.; Sturchio, N. C.; Winsor, L. *Org. Geochem.* **1999**, *30*, 755–763.
(14) Kim, Y. H.; Carraway, E. R. *Environ. Technol.* **2003**, *24*, 809–819.
(15) Arnold, W. A.; Roberts, A. L. *Environ. Sci. Technol.* **1998**, *32*, 3017–3025.
(16) Arnold, W. A.; Roberts, A. L. *Environ. Sci. Technol.* **2000**, *34*, 1794–1805.
(17) Roberts, A. L.; Totten, L. A.; Arnold, W. A.; Burris, D. R.; Campbell, T. J. *Environ. Sci. Technol.* **1996**, *30*, 2654–2659.
(18) Gillham, R. W.; O'Hannesin, S. F. *Ground Water* **1994**, *32*, 958–967.
(19) O'Hannesin, S. F.; Gillham, R. W. *Ground Water* **1998**, *36*, 164–170.
(20) Shimomura, T.; Sanford, R. A. *J. Environ. Qual.* **2005**, *34*, 1435–1438.
(21) Farrell, J.; Melitas, N.; Kason, M.; Li, T. *Environ. Sci. Technol.* **2000**, *34*, 2549–2556.
(22) Lowry, G. V.; Reinhard, M. *Environ. Sci. Technol.* **2000**, *34*, 3217–3223.
(23) Lowry, G. V.; Reinhard, M. *Environ. Sci. Technol.* **2001**, *35*, 696–702.
(24) Liu, Z.; Betterton, E. A.; Arnold, R. G. *Environ. Sci. Technol.* **2000**, *34*, 804–811.
(25) Lin, X. Q.; Boisselier-Cocolios, B.; Kadish, K. M. *Inorg. Chem.* **1986**, *25*, 3242–3248.

chlorinated ethylenes and other chlorocarbons using H_2 as the reductant.^{22,23,29–35} In these systems the noble metal is the catalyst and H_2 the reducing agent. We propose that metal hydrides play an active role in these systems, as H_2 is needed for degradation to occur. In order to probe this mechanistic hypothesis, we have explored the use of homogeneous rhodium hydrides as catalysts for the degradation of chlorinated ethylenes.

Heterogeneous rhodium-based catalysts have been used to dechlorinate chlorinated alkenes and alkanes. For example, Rh/alumina, Rh/ SiO_2 , or RhCl_3 catalysts in the presence of H_2 fully dechlorinate dichloropropane,³⁶ dichlorobutenes,³⁷ perchloroethylene,³⁸ trichloroethylene,²⁹ and 1,2-dichloroethane.^{29,39,40} However due to difficulties associated with studying reaction mechanisms in heterogeneous systems, little is known about the mechanism of these reactions.

There are also a few examples of homogeneous catalytic systems that use a phosphinorhodium catalyst and hydrogen to degrade chlorofluoromethanes⁴¹ and chloroalkanes.^{40,42} Furthermore, Esteruelas et al. employed chlorotris(triphenylphosphino)rhodium, $(\text{PPh}_3)_3\text{RhCl}$, as a homogeneous catalyst in the presence of triethylsilane (Et_3SiH) to dehalogenate chlorinated alicyclic⁴³ and aryl^{44,45} compounds (i.e., γ -hexachlorocyclohexane, chlorobenzene, and polychlorinated benzenes). The proposed first step of this reaction is the production of Et_3SiCl and $(\text{PPh}_3)_3\text{RhH}$ as the active catalytic intermediate, and for hexachlorocyclohexanes, an oxidative addition/ β -chloride elimination mechanism was proposed.⁴³

Phosphinorhodium complexes also catalytically activate sp^2 -hybridized C–F bonds, including fluorinated arenes^{46–51} and alkenes.^{52–56} In these systems, H_2 and various silanes have been employed as reducing agents, and alkyl and aryl phosphines have been used as ancillary ligands.^{46–56}

Previously, we reported that dehalogenation of vinyl fluoride, vinyl chloride, and chlorofluoroethylenes occurs in the presence of $(\text{PPh}_3)_3\text{RhCl}$ and Et_3SiH .⁵² This reaction was found to have an *intermolecular* preference for C–F bond activation versus C–Cl bond activation, with vinyl fluoride degrading the fastest of the substrates tested. The data also support an *intramolecular* preference for C–Cl bond activation versus C–F bond activation. Specifically, dehalogenation of chlorofluoroethylenes resulted in the observation of only vinyl fluoride and not vinyl chloride. The rate of dehalogenation increased with sequential halogen removal, such that dihaloalkenes were degraded slower than monohaloalkenes. The substitution pattern also affected the rates; 1,1-dihaloalkenes were degraded faster than the 1,2-dihaloalkenes. No isomerization of the 1,2-dichloroethylenes was observed during the dehalogenation. This system showed marked preference for sp^2 -hybridized C–X bonds versus sp^3 -hybridized bonds. Halogenated ethylenes were readily degraded under the conditions, but 1-fluorooctane, 1,1,2-trichloroethane, dichloromethane, and 1,2-dichloroethane were not. While this earlier study established substrate scope and preferences, a firm mechanistic understanding was not attained.

Herein we report further studies of the catalytic dehalogenation of halogenated ethylenes by $(\text{PR}_3)_3\text{RhCl}$. We expand on our preliminary communication of the dehalogenation reactions catalyzed by $(\text{PPh}_3)_3\text{RhCl}$ in the presence of Et_3SiH and investigate the dehalogenation using H_2 as the reducing agent. These two systems were found to exhibit significant differences. We propose mechanisms for the reduction with Et_3SiH and H_2 , which favor Rh(I) and Rh(III) pathways, respectively.

Experimental Procedures

General Considerations. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques or in a nitrogen-filled glovebox (MBraun Unilab). All solvents and reagents were purchased from commercial suppliers unless otherwise stated; solvents were dried prior to use. Benzene- d_6 and *p*-xylene were distilled from a sodium/benzophenone ketyl mixture under nitrogen and stored in a sealed flask. *cis*-1,2-Dichloroethylene, *trans*-1,2-dichloroethylene (TCI America), trichloroethylene, perchloroethylene, 1,1-dichloroethylene, dichloromethane (Sigma-Aldrich), 1,2-dichloroethane, and trichloroethane (Acros) were dried over CaCl_2 , vacuum transferred into a sealed flask, and stored in the dark over 4 Å molecular sieves. Tetrahydrofuran- d_8 was dried over 4 Å molecular sieves. Vinyl chloride and d_1 -triethylsilane (Et_3SiD) (Sigma-Aldrich), all fluorine-containing gases (SynQuest Laboratories, Inc.), H_2 (Airgas),

(26) Middeldorp, P. J. M.; Luijten, M. L. G. C.; Van De Pas, B. A.; Van Eekert, M. H. A.; Kengen, S. W. M.; Schraa, G.; Stams, A. J. M. *Biorem. J.* **1999**, *3*, 151–169.

(27) Mohn, W. W.; Tiedje, J. M. *Microbiol. Rev.* **1992**, *56*, 482–507.

(28) Smidt, H.; de Vos, W. M. *Annu. Rev. Microbiol.* **2004**, *58*, 43–73.

(29) Bozzelli, J. W.; Chen, Y.-M. *Chem. Eng. Commun.* **1992**, *115*, 1–11.

(30) Kovenklioglu, S.; Cao, Z.; Shah, D.; Farrauto, R. J.; Balko, E. N. *AIChE J.* **1992**, *38*, 1003–1012.

(31) Lowry, G. V.; Reinhard, M. *Environ. Sci. Technol.* **1999**, *33*, 1905–1910.

(32) McNab, W. W. Jr; Ruiz, R. *Chemosphere* **1998**, *37*, 925–936.

(33) McNab, W. W. Jr; Ruiz, R.; Reinhard, M. *Environ. Sci. Technol.* **2000**, *34*, 149–153.

(34) Nishijima, W.; Ochi, Y.; Tsai, T.-Y.; Nakano, Y.; Okada, M. *Appl. Catal., B* **2004**, *51*, 135–140.

(35) Schreier, C. G.; Reinhard, M. *Chemosphere* **1995**, *31*, 3475–3487.

(36) Scharfe, G.; Wilhelms, R. E. *Catalytic dechlorination of dichloropropane*. 71-2164074, 19711223, **1973**.

(37) Vojtko, J.; Hrusovsky, M. *Chem. Zvesti.* **1972**, *26*, 460–465.

(38) Ordóñez, S.; Sastre, H.; Diez, F. V. *Thermochim. Acta* **2001**, *379*, 25–34.

(39) Chang, C.-C.; Reo, C. M.; Lund, C. R. F. *Appl. Catal., B* **1999**, *20*, 309–317.

(40) Trabuco, E.; Ford, P. C. *J. Mol. Catal. A: Chem.* **1999**, *148*, 1–7.

(41) Cho, O.-J.; Lee, I.-M.; Park, K.-Y.; Kim, H.-S. *J. Fluorine Chem.* **1995**, *71*, 107–109.

(42) Kim, H.-S.; Cho, O.-J.; Lee, I.-M.; Hong, S.-P.; Kwag, C.-Y.; Ahn, B. S. *J. Mol. Catal. A: Chem.* **1996**, *111*, 49–65.

(43) Esteruelas, M. A.; Herrero, J.; Olivan, M. *Organometallics* **2004**, *23*, 3891–3897.

(44) Esteruelas, M. A.; Herrero, J.; Lopez, F. M.; Martin, M.; Oro, L. A. *Organometallics* **1999**, *18*, 1110–1112.

(45) Diaz, J.; Esteruelas, M. A.; Herrero, J.; Moralejo, L.; Olivan, M. *J. Catal.* **2000**, *195*, 187–192.

(46) Aizenberg, M.; Milstein, D. *Science* **1994**, *265*, 359–361.

(47) Aizenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 8674–8675.

(48) Young, R. J. Jr; Grushin, V. V. *Organometallics* **1999**, *18*, 294–296.

(49) Edelbach, B. L.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 7734–7742.

(50) Ishii, Y.; Chatani, N.; Yorimitsu, S.; Murai, S. *Chem. Lett.* **1998**, 157–158.

(51) Fuchibe, K.; Ohshima, Y.; Mitomi, K.; Akiyama, T. *J. Fluorine Chem.* **2007**, *128*, 1158–1167.

(52) Peterson, A. A.; McNeill, K. *Organometallics* **2006**, *25*, 4938–4940.

(53) Noveski, D.; Braun, T.; Schulte, M.; Neumann, B.; Stammer, H.-G. *Dalton Trans.* **2003**, 4075–4083.

(54) Braun, T.; Noveski, D.; Neumann, B.; Stammer, H.-G. *Angew. Chem., Int. Ed.* **2002**, *41*, 2745–2748.

(55) Braun, T.; Noveski, D.; Ahijado, M.; Wehmeier, F. *Dalton Trans.* **2007**, 3820–3825.

(56) Braun, T.; Wehmeier, F.; Altenhoener, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 5321–5324.

and deuterium (Matheson Gas Products, Inc.) were used as received. $(\text{PPh}_3)_3\text{RhCl}$,⁵⁷ $(\text{PPh}_3)_4\text{RhH}$,⁵⁸ $(\text{PPh}_3)_3\text{RhH}$,⁴³ $(\text{PPh}_3)_3\text{RhF}$,⁵⁹ $(\text{PMe}_3)_3\text{RhCl}$,⁶⁰ and $(\text{PEt}_3)_3\text{RhCl}$ ⁶⁰ were prepared according to literature procedures and characterized by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Dechlorination reactions were performed in sealed NMR tubes to prevent volatilization of reactants or products. NMR spectra were acquired on Varian UNITY Inova NMR spectrometers (300, 500, and 600 MHz) and referenced to the residual protiated solvent ($\text{C}_6\text{D}_5\text{H}$, 7.16 ppm). ^{19}F NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were acquired at 282.12 and 121.4 MHz, respectively, with ^{31}P referenced to 85% phosphoric acid and ^{19}F referenced to trichlorofluoromethane, both as external standards.

$[\text{P}(p\text{-FC}_6\text{H}_4)_3]_3\text{RhCl}$ and $[\text{P}(p\text{-MeOC}_6\text{H}_4)_3]_3\text{RhCl}$. These syntheses were modified from the procedure described by Montelatici et al.⁶¹ 1,5-Cyclooctadienerhodium(I) chloride dimer ($[(\text{COD})\text{RhCl}]_2$) was dissolved in toluene, and 3 molar equiv of the desired phosphine was added. The solution was left to stir for 14 h at ambient temperature. Complexes were purified by crystallization from toluene. Crystals were isolated by filtration and dried *in vacuo*. The complexes were characterized by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR and compared to the literature.⁶¹

Reaction Kinetics with Et_3SiH . Kinetic experiments were performed in sealed NMR tubes monitoring the reaction by ^1H NMR spectroscopy. The reaction mixture was kept frozen until immediately prior to placement in the NMR probe; NMR probe temperature was set to 35 or 55 °C. The kinetic data were collected in an arrayed experiment set to scan every 2 to 5 min. The rates of dehalogenation were determined by quantifying the disappearance of the substrate resonances, integrating versus internal standard *p*-xylene. These data were plotted as concentration of substrate versus time and fit to a first-order exponential decay function.

Relative Reaction Rates with H_2 . Substrate disappearance after 60 min was determined using sealed NMR tubes and monitoring the reaction by ^1H NMR spectroscopy. The reaction mixture was kept frozen until immediately prior to placement in the NMR probe; NMR probe temperature was set to 22 °C. A quantitative NMR spectrum was taken to determine the initial concentration of the substrate. The NMR tube was then immediately frozen in liquid nitrogen until ready to mix by inversion. The tube was thawed to room temperature and mixed by repeated inversion for 60 min, at a rate of 15 inversions per minute, and then frozen in liquid nitrogen. The final NMR spectrum was taken with the same parameters as the first NMR spectrum. The percentages of substrate dehalogenation were determined by quantifying the disappearance of the substrate resonances, integrating versus internal standard *p*-xylene, and determining the amount reacted by comparing the initial NMR and final NMR integration.

Dechlorination Using Et_3SiH . A stock solution containing $(\text{PPh}_3)_3\text{RhCl}$ (2.4 mM), Et_3SiH (125 mM), and *p*-xylene (3.3 mM; used as an internal standard) was prepared in C_6D_6 . An aliquot (700 μL) of this stock solution was added by syringe to a sealable NMR tube. The substrate was then either added via syringe in the glovebox or transferred as a gas on a Schlenk line using a known volume bulb. Kinetic data collection was performed as described above. Products of the dehalogenation reactions were determined by comparing the NMR resonances, chemical shifts, and coupling constants to authentic standards.

Dechlorination Using H_2 (or D_2) Gas. A stock solution containing $(\text{PPh}_3)_3\text{RhCl}$ (2.4 mM), NEt_3 (150 mM), and *p*-xylene

(3.3 mM; used as an internal standard) was prepared in C_6D_6 . An aliquot (700 μL) of this stock solution was added by syringe into a sealable NMR tube. The substrate was then either added via syringe in the glovebox or transferred as a gas on a Schlenk line using a known volume bulb. The headspace was evacuated from the tube by freezing the solution and placing it under vacuum. The mixture was warmed to room temperature, and the headspace was filled with approximately 1 atm of H_2 (or D_2). The tube was inverted three times to mix H_2 into the C_6D_6 and then immediately frozen in liquid nitrogen. Products of the dehalogenation reactions were determined by comparing the NMR resonances, chemical shifts, and coupling constants to authentic standards.

Dechlorination Using $(\text{PPh}_3)_4\text{RhH}$. A stock solution containing $(\text{PPh}_3)_4\text{RhH}$ (2.4 mM) and *p*-xylene (3.3 mM; used as an internal standard) was prepared in C_6D_6 . An aliquot (700 μL) of this stock solution was added by syringe into a sealable NMR tube. Substrate (20–30 mM) was added to this solution by syringe. The tube was mixed by inversion. Products and reaction progress was monitored using NMR spectroscopy at room temperature.

Dechlorination Using $(\text{PPh}_3)_3\text{RhH}$ (or $(\text{PPh}_3)_3\text{RhD}$). A procedure similar to the literature was adapted.⁴³ A solution containing $(\text{PPh}_3)_3\text{RhCl}$ (10 mM) and $\text{Et}_3\text{SiH}(\text{D})$ (30 mM) was prepared in C_6D_6 in a sealable NMR tube. The solvent and volatile materials were removed under vacuum on a Schlenk line. The solid was then redissolved in 700 μL of C_6D_6 in the sealable NMR tube, and an NMR spectrum was acquired to confirm only $(\text{PPh}_3)_3\text{RhH}(\text{D})$ was present. Substrate (20 mM) was then added to this solution by syringe. The tube was mixed by inversion. Products and reaction progress were monitored using NMR spectroscopy at room temperature.

$(\text{PPh}_3)_n\text{RhCl}$ for Use in Phosphine Ratio Experiments. The catalyst was prepared *in situ* as described above using $[(\text{COD})\text{RhCl}]_2$ and PPh_3 . Appropriate equivalents of triphenylphosphine were added to a 2.4 mM Rh solution with 1.7 mM *p*-xylene in C_6D_6 . The solutions were left overnight to react. The Et_3SiH (125 mM) and *cis*-DCE (30 mM) were added by syringe. The sealable NMR tubes were frozen immediately and stored in liquid nitrogen until inserted in the NMR probe. Kinetic data collection was performed as described above.

Results

Dechlorination Using Et_3SiH . Treatment of *cis*-1,2-dichloroethylene (*cis*-DCE, 30 mM in C_6D_6) with Et_3SiH (125 mM) and a catalytic amount of $(\text{PPh}_3)_3\text{RhCl}$ (2.4 mM) at 55 °C leads to complete dechlorination in 80 min ($t_{1/2}$ of 23 min) (eq 1). The reaction was monitored by ^1H NMR spectroscopy. The initial products observed were vinyl chloride and Et_3SiCl (eq 1). Vinyl chloride was quickly dechlorinated to ethylene. Over the course of the reaction, 1-butene and, eventually, *cis*- and *trans*-2-butene were also produced. After *cis*-DCE was fully degraded, a small amount of ethane was also observed. These results suggest that dechlorination to ethylene is followed by dimerization to 1-butene and ultimately isomerization to 2-butenes. These dimerization^{62,63} and isomerization^{64–66} reactions are known. The yield of observed products was essentially

(57) Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1990**, 28, 77–79.

(58) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1990**, 28, 81–83.

(59) Grushin, V. V.; Marshall, W. J. *J. Am. Chem. Soc.* **2004**, 126, 3068–3069.

(60) Price, R. T.; Andersen, R. A.; Muetterties, E. L. *J. Organomet. Chem.* **1989**, 376, 407–417.

(61) Montelatici, S.; van der Ent, A.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 1054–1058.

(62) Cramer, R. J. *Am. Chem. Soc.* **1965**, 87, 4717–4727.

(63) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711–1732.

(64) Tuner, M.; Von Jouanne, J.; Brauer, H. D.; Kelm, H. *J. Mol. Catal.* **1979**, 5, 433–445.

(65) Tuner, M.; Von Jouanne, J.; Brauer, H. D.; Kelm, H. *J. Mol. Catal.* **1979**, 5, 425–431.

(66) Tuner, M.; Von Jouanne, J.; Kelm, H. *J. Mol. Catal.* **1979**, 5, 447–457.

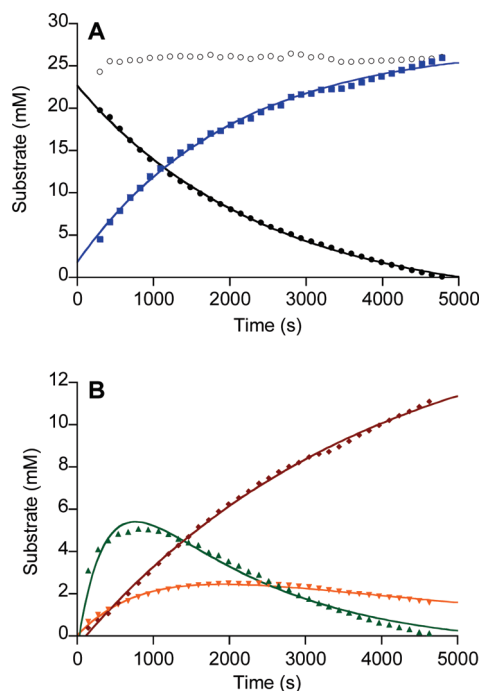
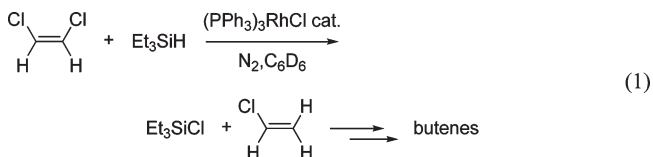


Figure 1. (A) *cis*-DCE degradation (●) by (PPh₃)₃RhCl (2.4 mM) and Et₃SiH (125 mM) at 55 °C and the subsequent appearance of reaction products (■ = sum of reaction products C₂ mass), as well as C₂ mass balance (○). (B) Growth of specific reaction products during the course of *cis*-DCE degradation: vinyl chloride (▲), ethylene (▼), butenes (◆). Data are fitted with first-order decay (*cis*-DCE), first-order exponential growth and decay (vinyl chloride and ethylene), and first-order exponential growth (butenes).

quantitative, as vinyl chloride, ethylene, and butenes comprise over 95% of the C₂ mass. The product yields were determined by ¹H NMR integration versus an internal standard, *p*-xylene.



To further characterize this C–Cl bond activation process, a study of the reaction kinetics was undertaken. Kinetic experiments were conducted in a temperature-controlled NMR probe, and concentrations of the reactants and products were determined by integration of the ¹H NMR resonances relative to those of the internal standard (*p*-xylene). Pseudo-first-order reaction kinetics were observed for the loss of *cis*-DCE under these reaction conditions. A sample kinetic plot depicting the exponential degradation of *cis*-DCE with concomitant growth of products is shown in Figure 1. The C₂ mass balance is also depicted.

All products were observed after 10 min of reaction time at 55 °C. This is consistent with fast degradation of the vinyl chloride intermediate.⁵² The dimerization and isomerization reactions occurred while chlorinated substrates were still present in the reaction mixture.

Recently we reported that dehalogenation of vinyl fluoride, vinyl chloride, and chlorofluoroethylenes occurs in the presence of (PPh₃)₃RhCl and Et₃SiH.⁵² Pseudo-first-order

Table 1. Observed Rate Constant of Substrate Degradation (*k*_{obs}) with Et₃SiH

substrate	<i>k</i> _{obs} (10 ^{−5} s ^{−1}) ^a	<i>k</i> _{rel} ^c
vinyl fluoride	50 ± 5 ^b	71.4
1,1-chlorofluoroethylene	24 ± 8 ^b	34.3
vinyl chloride	8 ± 1 ^b	11.4
1,1-DCE	4 ± 2 ^b	5.7
<i>cis</i> -DCE	2.7 ± 0.8 ^b	3.9
<i>trans</i> -DCE	2.5 ± 0.9	3.6
<i>cis</i> -1,2-chlorofluoroethylene	2.2 ± 0.3 ^b	3.1
<i>trans</i> -1,2-chlorofluoroethylene	1.7 ± 0.4 ^b	2.4
TCE	0.7 ± 0.3	1.0
PCE	< 0.1	< 0.1

^a Error is the standard deviation of the replicate experiments. Values were determined from loss of substrate versus time using ¹H NMR at 35 °C. Each sealable NMR tube contained substrate (20–30 mM), catalyst ((PPh₃)₃RhCl, 2.4 mM), Et₃SiH (125 mM), and internal standard (*p*-xylene, 3.3 mM) in C₆D₆. ^b Ref 52. ^c Relative rate constants (*k*_{rel}) are relative to the rate of dehalogenation of TCE (0.7 × 10^{−5} s^{−1}).

observed rate constants for those previously reported, as well as for *trans*-1,2-dichloroethylene (*trans*-DCE), TCE, and PCE, are compiled in Table 1. Reinforcing the previous conclusions about the reaction, the rate of dehalogenation was found to increase with sequential chlorine removal, such that PCE is degraded slowest, followed by TCE and the dihaloalkenes. The most facily degraded substrates were the monohaloalkenes. When comparing among the dichloroethylenes, the relative rates of degradation are very similar, with 1,1-dichloroethylene (1,1-DCE) reacting the fastest of the three.

Et₃SiCl was the major silane product observed during the dehalogenation reactions; however, it was not the only silane product observed, as hexaethyldisilane (Et₃Si-Si-Et₃) and vinyltriethylsilane (Et₃SiCHCH₂) were also observed. During the dechlorination of 1,1-DCE, TCE, and vinyl chloride, a small amount of Et₃SiCHCH₂ was observed by ¹H NMR spectroscopy. With all substrates, Et₃SiCHCH₂ was observed after the halogenated substrates were completely consumed in the catalytic reaction. This suggests that the Et₃SiCHCH₂ is produced from ethylene and some substrates inhibit its formation. This was tested by reacting ethylene under the dehalogenation reaction conditions. When ethylene was reacted with (PPh₃)₃RhCl and Et₃SiH under identical reaction conditions, Et₃SiCHCH₂, ethane, and Et₃SiCl (small amount from loss of Cl from (PPh₃)₃RhCl) were observed.

Experiments were performed to determine the reaction order in catalyst, (PPh₃)₃RhCl, and Et₃SiH. Dechlorination was found to be first-order in catalyst, (PPh₃)₃RhCl, at concentrations ranging from 0.1 to 2.4 mM (Figure 2). This was determined by measuring the initial rates of *cis*-DCE degradation under pseudo-first-order reaction conditions at 55 °C in the presence of a constant amount of Et₃SiH (125 mM) and varying amounts of catalyst. The reaction was found to be zero-order in Et₃SiH by measuring the pseudo-first-order *k*_{obs} for *cis*-DCE degradation at 55 °C and monitoring the reaction by ¹H NMR spectroscopy. The studies were conducted with Et₃SiH (20–300 mM) and (PPh₃)₃RhCl (2.4 mM) (Figure 3). The rate of rhodium-mediated dechlorination does not depend on Et₃SiH concentrations when concentrations above 20 mM are used.

Dehalogenation Using Dihydrogen. Dihydrogen, H₂, was also used as the reducing agent for catalytic dehalogenation. Treatment of *cis*-DCE (30 mM in C₆D₆) with (PPh₃)₃RhCl

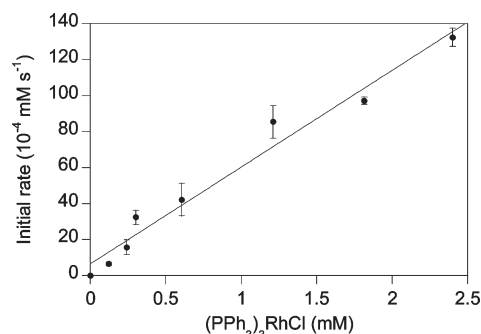


Figure 2. Observed degradation rate of *cis*-DCE in the presence of 125 mM Et_3SiH and varying concentrations of catalyst (0.1 to 2.4 mM) in C_6D_6 . Values were determined using initial rates for loss of substrate as monitored by ^1H NMR at 55 $^\circ\text{C}$. The fit is linear to the initial rate data, $R^2 = 0.9721$. Error bars were determined from the standard error in the linear fit of the initial rate plots.

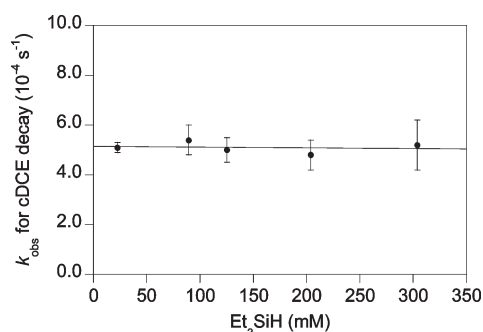
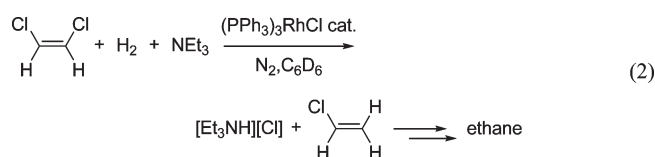


Figure 3. Observed *cis*-DCE degradation (k_{obs}) in the presence of 2.4 mM $(\text{PPh}_3)_3\text{RhCl}$ and varying concentrations of Et_3SiH (from 22 to 300 mM) in C_6D_6 . Error bars were determined from the standard error in the exponential fit to the substrate decay kinetic plots, except when the Et_3SiH concentration was 125 mM, in which case the error is the standard deviation of 11 experiments.

(2.4 mM) and H_2 (1 atm) at room temperature resulted in complete dechlorination after 80 min (eq 2). In this case, NEt_3 (150 mM) was added to scavenge the resulting HCl . In the absence of NEt_3 , catalyst degradation and formation of $[\text{HPPH}_3][\text{Cl}]$ were observed. The reaction was mixed by inverting continuously until analyzed. The suite of products observed from dehalogenation using H_2 was similar to that observed using Et_3SiH . Initially, vinyl chloride and ethylene were produced. However, unlike the Et_3SiH system, no butenes were observed. Hydrogenation was observed during the dechlorination reaction, resulting in ethane and a small amount of 1,2-dichloroethane and 1-chloroethane. In all cases, 93% of the C_2 mass was accounted for. The 1,2-dichloroethane and 1-chloroethane products account for 2% of the C_2 mass balance.



The relative reactivity of $(\text{PPh}_3)_3\text{RhCl}$ with halogenated substrates was further examined using H_2 as the reducing

Table 2. Substrate Degradation Rates with H_2 as the Reductant^a

substrate	percent reacted (%)	k_{rel}^b
vinyl chloride	75 ± 1	10.2
<i>cis</i> -DCE	75 ± 3	10.1
<i>trans</i> -DCE	44 ± 4	4.2
1,1-DCE	31 ± 6	2.7
TCE	13 ± 8	1.0

^a Percent reacted values were determined from loss of substrate after 60 min of constant inversion using quantitative ^1H NMR spectroscopy at room temperature, 22 $^\circ\text{C}$. Each sealable NMR tube contained substrate (20–30 mM), catalyst $(\text{PPh}_3)_3\text{RhCl}$ (2.4 mM), H_2 (1 atm), NEt_3 (150 mM), and internal standard (*p*-xylene, 3.3 mM) in C_6D_6 . The estimated error is the standard deviation of three trials. ^b Relative rate constants were determined assuming a first-order degradation model and were normalized to the rate of TCE degradation.

agent. Kinetic studies in the NMR probe were not conducted due to the low solubility of H_2 in C_6D_6 and slow mass transfer kinetics, which made it difficult to maintain pseudo-first-order conditions. The substrates were compared by quantifying substrate lost after 60 min of reaction at room temperature. Each reaction mixture consisted of substrate (20–30 mM), $(\text{PPh}_3)_3\text{RhCl}$ (2.4 mM), and NEt_3 (150 mM); the headspace in the NMR tube was filled with H_2 at 1 atm. The percent reacted after 60 min was calculated for the chlorinated ethylenes and is compiled in Table 2. The general reactivity trends were the same as when Et_3SiH was employed. The rate of dechlorination increases with loss of chlorine substituents, as vinyl chloride degraded the fastest and TCE the slowest. However, unlike the Et_3SiH system, *cis*-DCE is degraded at a similar rate to vinyl chloride, while 1,1-DCE and *trans*-DCE degraded at a slower rate. All of the dichloroethylenes produce vinyl chloride as a reactive intermediate, which was then dechlorinated to ethylene and further hydrogenated to ethane. When ethylene was reacted as the substrate in this system (with H_2 , NEt_3 , and $(\text{PPh}_3)_3\text{RhCl}$), hydrogenation occurs, and ethane is observed.

The reaction was found to be first-order in catalyst, $(\text{PPh}_3)_3\text{RhCl}$, when H_2 was used as the hydride source. The fraction of *cis*-DCE degraded in 60 min versus catalyst concentration (0 to 2.4 mM) is depicted in Figure 4. The data are plotted on a logarithmic scale, which should linearize the data set if the reaction is pseudo-first-order and first-order in catalyst. Indeed, a linear relationship is observed (Figure 4). There is no effect on the percent *cis*-DCE degraded in 60 min when varying the concentration of NEt_3 from 50 to 200 mM when the amount of $(\text{PPh}_3)_3\text{RhCl}$ was kept constant (2.4 mM) (Figure 5).

When vinyl fluoride (25 mM) is reacted with $(\text{PPh}_3)_3\text{RhCl}$ (2.4 mM) and H_2 (1 atm) in the presence of NEt_3 (150 mM), the major reaction pathway is hydrogenation, as the major product is fluoroethane and the minor product ethylene. Because defluorination was not the major degradation pathway, the percent reacted in 60 min is not included in Table 2.

Fluoroethane and ethylene were observed from the reaction of vinyl fluoride with independently prepared $(\text{PPh}_3)_3\text{RhF}^{59}$ and H_2 . This observation is consistent with $(\text{PPh}_3)_3\text{RhF}$ being a potential intermediate in the catalytic cycle.

Chlorofluoroethylenes were reacted with $(\text{PPh}_3)_3\text{RhCl}$, H_2 , and NEt_3 . The first product observed was vinyl fluoride, and no vinyl chloride was detected during the dehalogenation, similar to the Et_3SiH system. Some hydrogenation product, chlorofluoroethane, was also observed. The major final product was fluoroethane, the hydrogenation product of the vinyl fluoride.

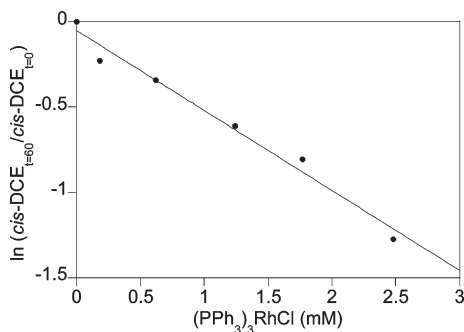


Figure 4. Natural log of the fraction of *cis*-DCE degraded in 60 min versus catalyst concentration. Reaction conditions: 22 ± 1 °C, 1 atm H_2 , 150 mM NEt_3 , and varying concentration of catalyst (0 to 2.4 mM) in C_6D_6 . The fit is linear to the data, $R^2 = 0.9799$.

Sp^3 -Hybridized Carbon–Halogen Bonds. Similar to Et_3SiH , when H_2 is used as the reducing agent under identical reaction conditions, there is no reaction with 1,2-chloroethane or dichloromethane after two days at room temperature.

NMR Observation of Intermediates. When Et_3SiH and $(\text{PPh}_3)_3\text{RhCl}$ were combined in a 1:1 or 2:1 ratio, a new ^1H NMR resonance consistent with a Rh-H species was observed at -7.9 ppm. Esteruelas et al. observed the same result and assigned the resonance to $(\text{PPh}_3)_3\text{RhH}$.^{43,67} In our system, when excess Et_3SiH (> 10 equiv) is allowed to react with $(\text{PPh}_3)_3\text{RhCl}$, the only rhodium hydride complex observed initially is $(\text{PPh}_3)_2\text{RhH}(\text{Cl})\text{SiEt}_3$, identified by the upfield hydride resonance ($\delta -14.7$, $J_{\text{Rh-H}} = 22$ Hz) in the $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum and its $^{31}\text{P}\{^1\text{H}\}$ resonance ($\delta 39.7$, d, $J_{\text{Rh-P}} = 128$ Hz).⁶⁸ With time, the $(\text{PPh}_3)_2\text{RhH}(\text{Cl})\text{SiEt}_3$ ^1H resonance at -14.7 ppm disappears, and the $(\text{PPh}_3)_3\text{RhH}$ resonance, -7.9 ppm, appears.⁶⁷ The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows the same behavior, with the $(\text{PPh}_3)_2\text{RhH}(\text{Cl})\text{SiEt}_3$ doublet at 39.7 ppm giving way to the $(\text{PPh}_3)_3\text{RhH}$ doublet at 42 ppm (158 Hz). We propose that the solution of Et_3SiH and $(\text{PPh}_3)_3\text{RhCl}$ is in equilibrium, such that $\text{L}_n\text{Rh}(\text{I})\text{-H}$ and $\text{L}_n\text{Rh}(\text{III})\text{-H}$ complexes are present during the catalytic cycle. This is supported by the $^{31}\text{P}\{^1\text{H}\}$ NMR resonances observed during dechlorination reactions; both $(\text{PPh}_3)_2\text{RhH}(\text{Cl})\text{-SiEt}_3$ ($\delta 39.2$, d, $J_{\text{Rh-P}} = 130$ Hz) and $(\text{PPh}_3)_3\text{RhH}$ ($\delta 42$, d, $J_{\text{Rh-P}} = 156$ Hz) are observed. This differs from observations made by Esteruelas et al. during the dechlorination of hexachlorocyclohexane. They reported a doublet at 39.4 ppm (115 Hz) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum and two hydride peaks in the ^1H NMR spectra (-9.38 and -16.73 ppm) that they assigned to $(\text{PPh}_3)_3\text{RhH}_2\text{Cl}$.^{43,63,69}

$(\text{PPh}_3)_3\text{RhH}$ can be isolated by reacting $(\text{PPh}_3)_3\text{RhCl}$ with excess Et_3SiH and then removing Et_3SiCl and unreacted Et_3SiH under vacuum. $(\text{PPh}_3)_3\text{RhH}$ isolated in this way was found to react immediately with *cis*-DCE to yield vinyl chloride and ethylene, as well as $(\text{PPh}_3)_3\text{RhCl}$. Furthermore, independently synthesized and isolated $(\text{PPh}_3)_4\text{RhH}$ (2.4 mM) reacted readily with *cis*-DCE (20 mM) in C_6D_6 upon mixing at room temperature. $(\text{PPh}_3)_3\text{RhCl}$ and free PPh_3 were formed in these reactions, as indicated by $^{31}\text{P}\{^1\text{H}\}$

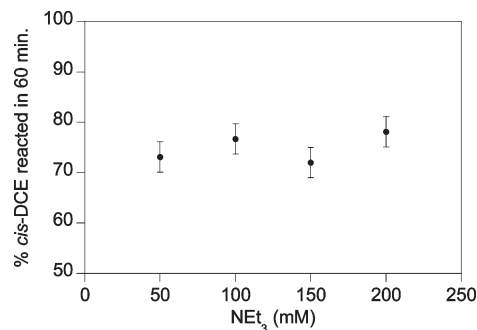


Figure 5. Percent *cis*-DCE degraded in 60 min at room temperature in the presence of H_2 (1 atm), $(\text{PPh}_3)_3\text{RhCl}$ (2.4 mM), and varying concentrations of NEt_3 (50 to 200 mM) in C_6D_6 . Values were determined by calculating loss of substrate using ^1H NMR at 22 °C. Error bars are set to 3%, which is based on the standard deviation of triplicate *cis*-DCE degradation.

NMR spectroscopy. The dechlorination products produced were ethylene and vinyl chloride, and 90% of the C_2 mass was accounted for by these products and unreacted *cis*-DCE.

When H_2 (1 atm) was reacted with $(\text{PPh}_3)_3\text{RhH}_2\text{Cl}$,^{43,63,69} was produced. This was indicated by ^1H NMR resonances observed at -9.4 and -16.7 ppm. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contained a doublet at 39.4 ppm (116 Hz) and a broad peak at 20 ppm. During the dehalogenation reactions with H_2 and $(\text{PPh}_3)_3\text{RhCl}$, the major species observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy was $(\text{PPh}_3)_3\text{RhH}_2\text{Cl}$. A small amount of $(\text{PPh}_3)_3\text{RhCl}$ and $(\text{PPh}_3)_2\text{RhCl}(\text{alkene})$ (36.6 ppm, 129 Hz)⁷⁰ were also observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. No resonances attributable to $(\text{PPh}_3)_3\text{RhH}$ were observed in either ^1H or $^{31}\text{P}\{^1\text{H}\}$ NMR spectra.

Effect of Phosphine:Rhodium Ratio on Rate. The phosphine dependence of the dechlorination of *cis*-DCE was explored in order to gain insight into the active catalytic species and to determine the optimum rhodium to phosphine ratio for *in situ* catalyst generation. Reactions were performed with *cis*-DCE (30 mM) and Et_3SiH (125 mM). The catalyst was formed *in situ* by mixing PPh_3 with $[(\text{COD})\text{RhCl}]_2$ at various ratios from 1:0 to 1:5 Rh: PPh_3 . The total Rh and Et_3SiH concentrations were kept constant in all experiments, and the amount of PPh_3 was varied accordingly. The effect of phosphine concentration on the rate constant was determined by measuring the pseudo-first-order k_{obs} for *cis*-DCE degradation at 55 °C using ^1H NMR spectroscopy.

The optimal rate constant was achieved with 3 equiv of phosphine. The reaction rate constant decreased with additional phosphine (Figure 6), and no dehalogenation was observed in the absence of phosphine. This result differs from previous reports on hydrogenation and dechlorination reactions where an initial ligand dissociation step is thought to produce $(\text{PPh}_3)_2\text{RhCl}$, with a 2:1 PPh_3 :Rh ratio, yielding the optimal rate of reaction (eq 3).^{43,61,63,71}



The inhibitory effect of greater than 3 equiv of phosphine was further verified in an independent experiment where 1 equiv of PPh_3 was added to a reaction mixture containing

(67) Strauss, S. H.; Diamond, S. E.; Mares, F.; Shriver, D. F. *Inorg. Chem.* **1978**, *17*, 3064–3068.

(68) Duckett, S. B.; Galvez-Lopez, M.-D.; Perutz Robin, N.; Schott, D. *Dalton Trans.* **2004**, 2746–2749.

(69) Duckett, S. B.; Newell, C. L.; Eisenberg, R. *J. Am. Chem. Soc.* **1994**, *116*, 10548–10556.

(70) Naaktgeboren, A. J.; Nolte, R. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1980**, *102*, 3350–3354.

(71) Ohtani, Y.; Fujimoto, M.; Yamagishi, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1453–1459.

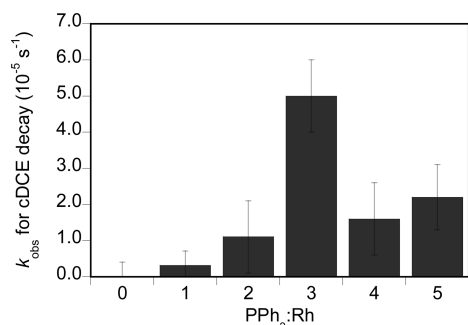


Figure 6. Observed rate constants (k_{obs}) for *cis*-DCE degradation are compared to the phosphine:rhodium ratio for the reaction of *cis*-DCE with Et_3SiH and the catalyst at 55 °C in C_6D_6 . In these studies, the catalyst was made from the *in situ* reaction of $[(\text{COD})\text{RhCl}]_2$ with PPh_3 . Error bars are the error in the exponential fit of the ^1H NMR data.

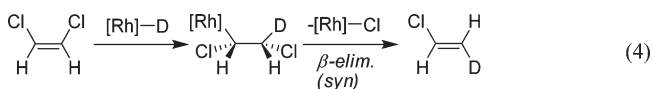
Et_3SiH , *cis*-DCE, and $(\text{PPh}_3)_3\text{RhCl}$. Under these conditions, a 3-fold decrease in the observed rate constant was observed compared to the same experiment without added phosphine. A similar result was also observed by Esteruelas et al. for chlorinated benzene dechlorination.^{43,44}

The *cis*-DCE degradation rate constant, k_{obs} , for *in situ* generated $(\text{PPh}_3)_3\text{RhCl}$ ($\text{PPh}_3:\text{Rh}$ ratio of 3:1) was an order of magnitude lower than when the reaction was performed with isolated and purified $(\text{PPh}_3)_3\text{RhCl}$. The source of this discrepancy was found to be 1,5-cyclooctadiene, which acted as an inhibitor for *cis*-DCE dechlorination by $(\text{PPh}_3)_3\text{RhCl}$ and Et_3SiH (data not shown).

In the H_2 system, the percentage of *cis*-DCE dechlorinated in 60 min in the presence of $(\text{PPh}_3)_3\text{RhCl}$ (2.4 mM), NEt_3 (150 mM), 1 equiv of PPh_3 (2.4 mM), and H_2 (1 atm) was found to be $42 \pm 6\%$. This was a relative decrease of 2.5 times compared to the reaction without the extra equivalent of PPh_3 , signifying that the addition of PPh_3 inhibited dechlorination of *cis*-DCE when H_2 was used.

Effect of Phosphine Structure on Rate. We also examined the effect of the electronic nature of the phosphine used in $(\text{PR}_3)_3\text{RhCl}$ on the reaction kinetics with *cis*-DCE and Et_3SiH by preparing $(\text{PPh}_3)_3\text{RhCl}$ analogues with trimethylphosphine, triethylphosphine, tris(*p*-methoxyphenyl)phosphine, and tris(*p*-fluorophenyl)phosphine. The observed rate of reaction with *cis*-DCE decreased monotonically with the basicity of the phosphine, with $[\text{P}(\text{FC}_6\text{H}_4)_3]\text{RhCl}$ being the most active (Table 3), while $(\text{PMe}_3)_3\text{RhCl}$ and $(\text{PEt}_3)_3\text{RhCl}$ complexes were found to be inactive. This trend was also observed by Montelatici et al. for the activation of hydrogen by $(\text{PPh}_3)_2\text{RhX}(\text{C}_6\text{H}_6)$.⁶¹ It was proposed that this was due to both steric and electronic reasons.⁶¹

Isotope Labeling. Our leading hypothesis for the dehalogenation process is an insertion/ β -chloride elimination mechanism. The first step of this mechanism involves insertion of the alkene into the $\text{Rh}-\text{H}$ bond, yielding a β -chloroalkyl complex, which then undergoes *syn*- β -chloride elimination. This process gives rise to stereospecific incorporation of the hydride-derived hydrogen. This mechanism is illustrated in eq 4.



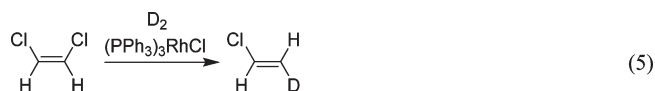
To test this mechanistic hypothesis, an experiment was performed using D_2 as the hydride source with $(\text{PPh}_3)_3\text{RhCl}$

Table 3. Rate Constants Obtained for Various $(\text{PR}_3)_3\text{RhCl}$ Complexes with *cis*-DCE and Et_3SiH and the Corresponding Phosphine Properties⁷²

isolated catalyst	k_{obs} (10^{-4} s^{-1}) 35 °C	k_{obs} (10^{-4} s^{-1}) 55 °C	$\text{p}K_{\text{a}}$ (PR_3H^+)	cone angle θ
$[\text{P}(\text{FC}_6\text{H}_4)_3]\text{RhCl}$	1.9 ± 0.7	n.d. ^a	1.97	145
$(\text{PPh}_3)_3\text{RhCl}$	0.27 ± 0.08	5.0 ± 0.5	2.73	145
$[\text{P}(p\text{-MeO-C}_6\text{H}_4)_3]\text{RhCl}$	n.d. ^a	0.40 ± 0.02	4.59	145
$(\text{PEt}_3)_3\text{RhCl}$	< 0.01	< 0.01	8.69	132
$(\text{PMe}_3)_3\text{RhCl}$	< 0.01	< 0.01	8.65	118

^a n.d. = not determined.

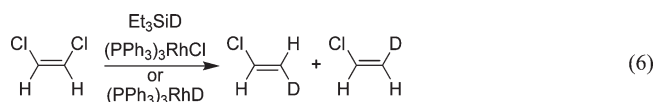
and *cis*-DCE. The *syn*- β -chloride elimination product, *E*-1-chloro-2-deuteroethylene ($J_{\text{H}-\text{H}} = 15 \text{ Hz}$), was observed in the ^1H NMR spectrum (eq 5) as hypothesized. No other chlorodeuteroethylenes were observed. These results, along with the reaction preferences previously discussed, support an insertion/*syn*- β -chloride elimination mechanism when hydrogen is used as the hydride source. This is also the only product observed when either Et_3SiCl or Et_3N was added to the reaction mixture of *cis*-DCE, D_2 , and $(\text{PPh}_3)_3\text{RhCl}$, indicating that these species play no role in the β -Cl elimination product formed.



A similar result was obtained in the reaction of *trans*-DCE with $(\text{PPh}_3)_3\text{RhCl}$ and D_2 in C_6D_6 . Only resonances for the *syn*- β -chloride elimination product were observed, *Z*-1-chloro-2-deuteroethylene ($J_{\text{H}-\text{H}} = 7 \text{ Hz}$).

However, in a similar experiment using Et_3SiD with $(\text{PPh}_3)_3\text{RhCl}$ and *cis*-DCE, a 1:1 mixture of *E*- and *Z*-1-chloro-2-deuteroethylene was observed in the ^1H NMR spectrum, as previously reported (eq 6).⁵² When isolated $(\text{PPh}_3)_3\text{RhD}$ was reacted with *cis*-DCE, the same 1:1 mixture of products was observed (eq 6). Switching solvents to tetrahydrofuran- d_8 , for the reaction of Et_3SiD with $(\text{PPh}_3)_3\text{RhCl}$ and *cis*-DCE, changed the product ratio to a 1:7 mixture of *E*- and *Z*-1-chloro-2-deuteroethylene.

Fully protonated (undeuterated) vinyl chloride is also observed with time in the Et_3SiD reaction and when the $(\text{PPh}_3)_3\text{RhD}$ is reacted with *cis*-DCE. The independent reaction of vinyl chloride with Et_3SiD and $(\text{PPh}_3)_3\text{RhCl}$ resulted in no deuterium incorporation into the residual vinyl chloride. This indicates that vinyl chloride is not isomerized under these conditions.



When the $(\text{PPh}_3)_3\text{RhCl}/\text{Et}_3\text{SiD}$ system was treated with *trans*-DCE, a 1:1.5 ratio of *E*- to *Z*-1-chloro-2-deuteroethylene was observed. The same product ratio (1:1.5, *E*:*Z*) was also observed when $(\text{PPh}_3)_3\text{RhD}$ was reacted with *trans*-DCE.

Discussion

Proposed Mechanism. The data for dehalogenation of halogenated ethylenes using $(\text{PPh}_3)_3\text{RhCl}$ with Et_3SiH and H_2 support similar, yet distinct, mechanisms for the two

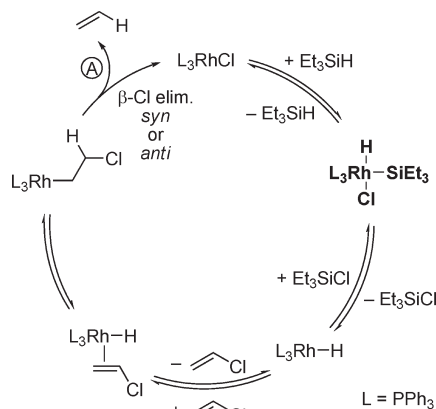


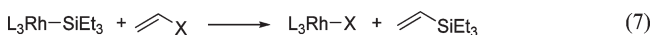
Figure 7. Proposed mechanism for the catalytic dehalogenation of chlorinated and fluorinated ethylenes using $(\text{PPh}_3)_3\text{RhCl}$ and Et_3SiH . The product elimination step is labeled A. It is proposed that reduction with Et_3SiH occurs primarily through a Rh(I) pathway, and the Rh(III) complex is highlighted in boldface.

reducing agents. The Et_3SiH and H_2 systems are characterized by four major differences:

1. Hydride complexes observed during reaction
2. Stereochemistry of elimination
3. Occurrence of hydrogenation/hydrosilylation products
4. Vinyl fluoride products

We propose two mechanisms that account for these differences, with the key distinction between them being that reduction with Et_3SiH occurs through a Rh(I)-type pathway (Figure 7), while the H_2 reduction occurs through a Rh(III)-type pathway (Figure 8). The mechanisms are presented first, followed by a discussion of how they account for each of the observations in the Et_3SiH and H_2 systems.

In the proposed mechanism, illustrated using vinyl chloride, when Et_3SiH is employed, the first step is oxidative addition of Et_3SiH to $(\text{PPh}_3)_3\text{RhCl}$ to form $(\text{PPh}_3)_3\text{RhH}(\text{Cl})\text{SiEt}_3$, which undergoes reductive elimination of Et_3SiCl , to give $(\text{PPh}_3)_3\text{RhH}$. Alkene association with $(\text{PPh}_3)_3\text{RhH}$ followed by insertion into the Rh–H bond leads to a Rh-alkyl complex. The alkyl complex may then undergo $\beta\text{-X}$ elimination (step A), yielding the dehalogenated alkene as well as the return of the catalyst $(\text{PPh}_3)_3\text{RhX}$ (Figure 7). This Rh-alkyl complex can undergo either *syn*- or *anti*- $\beta\text{-X}$ elimination, consistent with the D-labeling data, as described in the stereochemistry of elimination section below. We have depicted the Rh-alkyl complex as a tris(triphenylphosphine) complex; however, there is no direct evidence for this. Elimination could occur from, for example, bis- or tris-phosphine complexes. The observation of $\text{Et}_3\text{SiCHCH}_2$ suggests the possibility that a similar minor pathway involving $(\text{PPh}_3)_3\text{Rh-SiEt}_3$ may exist (eq 7).



The observation of $\text{Et}_3\text{Si-SiEt}_3$ lends credence to the presence of Rh-silyl species, as these are known intermediates in dehydrocoupling of silanes.^{73–77}

(72) Rahman, M. M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, 6, 650–658.

(73) Goikhman, R.; Milstein, D. *Chem.–Eur. J.* **2005**, 11, 2983–2988.

(74) Brown-Wensley, K. A. *Organometallics* **1987**, 6, 1590–1591.

(75) Rosenberg, L.; Davis, C. W.; Yao, J. J. *Am. Chem. Soc.* **2001**, 123, 5120–5121.

(76) Mitchell, G. P.; Tilley, T. D. *Organometallics* **1998**, 17, 2912–2916.

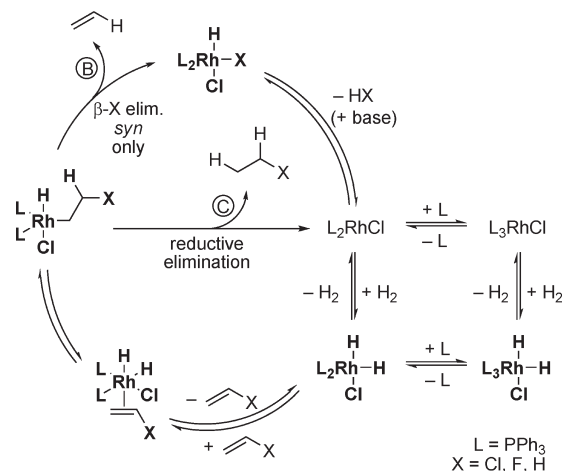
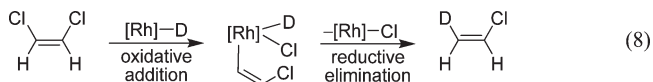


Figure 8. Proposed mechanism for the catalytic dehalogenation of chlorinated and fluorinated ethylenes using $(\text{PPh}_3)_3\text{RhCl}$ and H_2 . It is proposed that reduction with H_2 occurs primarily through a Rh(III) pathway with two possible product-forming reactions: *syn*- $\beta\text{-X}$ -elimination (B) and reductive elimination (C). All Rh(III) complexes are highlighted in boldface.

With fluorinated alkenes, the same mechanism is proposed. However, following $\beta\text{-F}$ -elimination $(\text{PPh}_3)_3\text{RhF}$ is generated. This species has been shown to be a competent catalyst.⁵²

When H_2 is used, the dominant pathway is proposed to be the Rh(III)-H pathway. Here, the initial step in the reaction is oxidative addition of H_2 to $(\text{PPh}_3)_3\text{RhCl}$ (either before or after phosphine dissociation). Alkene association at the open coordination site of $(\text{PPh}_3)_2\text{RhH}_2\text{Cl}$ followed by insertion into one of the Rh(III)–H bonds leads to a Rh-alkyl complex (Figure 8). From here, reductive elimination (step C, Figure 8) yields hydrogenation products, and *syn*- $\beta\text{-X}$ elimination (step B, Figure 8) yields dehalogenation products. As shown, the chloro ligand remains bound to the Rh throughout. Not shown explicitly is the hydrodehalogenation process that leaves the haloalkene halogen bound to the rhodium. In the case of fluoro substituents, this produces $(\text{PPh}_3)_2\text{RhF}$. We have verified that $(\text{PPh}_3)_3\text{RhF}$ is also a competent catalyst using H_2 as the reducing agent.

C–X Oxidative Addition Mechanism. Before considering in detail how the proposed mechanism accounts for the experimental observations, it is worth pointing out how the data do not support an alternative mechanistic hypothesis involving C–X oxidative addition (eq 8).



In an oxidative addition/reductive elimination mechanism, isotopic labeling studies would be expected to show retention of stereochemistry (eq 8). In fact, the isotopic labeling studies show inversion (with D_2) and scrambling (with Et_3SiD). Oxidative addition is also expected to show a preference for weaker sp^3 -hybridized C–X bonds over sp^2 -hybridized C–X bonds, as well as similar reactivity toward vinyl C–X and aryl C–X bonds. Neither was observed. Vinyl fluoride was degraded faster than vinyl chloride, which is also contrary to the expectations of an oxidative addition

(77) Turculet, L.; Feldman, J. D.; Tilley, T. D. *Organometallics* **2004**, 23, 2488–2502.

mechanism, as insertion into C–F bonds is more difficult than C–Cl insertion. Finally, the observation of hydrogenation products when H₂ is used as the reducing agent also supports insertion of the alkene into a Rh–H bond.

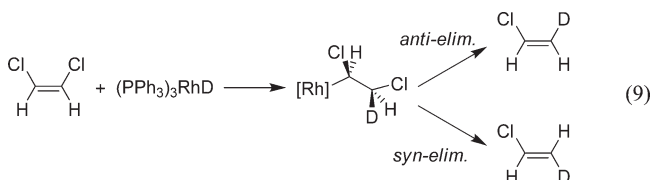
Hydride Complexes Observed during Reaction. Numerous lines of evidence support the intermediacy of rhodium hydride species in both the Et₃SiH and H₂ dehalogenation processes. First, conditions that produce Rh–H species were needed for dehalogenation. In the Et₃SiH system, no reaction was observed when *cis*-DCE was treated with either Et₃SiH or (PPh₃)₃RhCl alone. Similarly in the H₂ catalytic system, no reaction occurs when *cis*-DCE was reacted with either (PPh₃)₃RhCl or H₂ alone. Both (PPh₃)₃RhCl and either Et₃SiH or H₂ need to be present for reaction to occur. Second, the isolated Rh–H complex, (PPh₃)₄RhH, reacts directly with the halogenated ethylenes to give dehalogenation products. Finally, Rh–H complexes were observed during the dehalogenation reactions by ¹H NMR spectroscopy.

However, the spectroscopic data suggest that H₂ and Et₃SiH favor different pathways. During the course of the dehalogenation reactions with Et₃SiH, the Rh(I) hydride, (PPh₃)₃RhH, is the primary hydride species observed. Under H₂, both ¹H and ³¹P{¹H} NMR spectra show that the Rh(III) complex, (PPh₃)₃RhH₂Cl, is present. Presumably, the difference in the two systems is the strong driving force for reductive elimination of Et₃SiCl (or Et₃SiF in defluorination reactions) which pushes the silane system toward (PPh₃)₃RhH.

Stereochemistry of Elimination. When D₂ is reacted with (PPh₃)₃RhCl and *cis*-DCE or *trans*-DCE, the stereochemistry of the 1-chloro-2-deuteroethylene products (*E*-1-chloro-2-deuteroethylene or *Z*-1-chloro-2-deuteroethylene, respectively) is consistent with exclusive *syn*-β-Cl-elimination (step B, Figure 8).

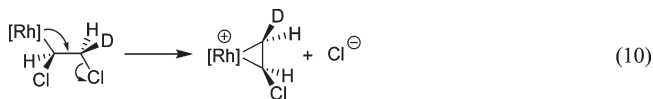
When Et₃SiD is reacted with (PPh₃)₃RhCl and *cis*-DCE in C₆D₆, a 1:1 mixture of *E*- to *Z*-1-chloro-2-deuteroethylene is observed, and when *trans*-DCE is reacted, a slightly different product ratio of 1:1.5 (*E*:*Z*) is observed. The same product ratios are observed when (PPh₃)₃RhD is used as the Rh–D source, supporting the conclusion that Et₃SiD/H follows a Rh(I)–H pathway (step A, Figure 7).

The mixture of *syn*- and *anti*-elimination products with Et₃SiH rules out the possibility that it reacts by the same pathway as H₂. Furthermore, spectroscopic evidence shows a mixture of Rh(III)–H and Rh(I)–H species with Et₃SiH and only Rh(III)–H with H₂. Taken together, the data suggest that β-haloalkyl complexes of Rh(III) give exclusively *syn*-elimination products, while β-haloalkyl complexes of Rh(I) can give both *syn*- and *anti*-elimination products (eq 9). This is based on experiments with (PPh₃)₃RhD and *cis*-DCE that show a 1:1 mixture of *E*-1-chloro-2-deuteroethylene and *Z*-1-chloro-2-deuteroethylene. In this system, it seems unlikely that Rh(III) species are involved and that both products come from the same dichloroethylrhodium(I) intermediate.



We speculate that the nucleophilicity of the metal center enhances the favorability of the *anti*-elimination pathway with Rh(I) over Rh(III). Pseudobackside displacement of the

leaving group by rhodium would lead directly to an alkene complex (eq 10).



A noteworthy difference between the proposed *syn*- and *anti*-elimination pathways is that significant charge buildup is expected in the *anti*-elimination pathway en route to the product ion pair. No such charge separation is expected in the *syn*-β-Cl-elimination pathway. Support for this model was obtained by switching to a more polar solvent. Reacting *cis*-DCE with Et₃SiD and (PPh₃)₃RhCl in tetrahydrofuran-*d*₈ resulted in a product ratio of 1:7 *E*- to *Z*-1-chloro-2-deuteroethylene, contrasting the 1:1 ratio observed in C₆D₆. We propose that the shift to increased amounts of the *anti*-elimination product (*Z*-1-chloro-2-deuteroethylene) is due to better stabilization of the *anti*-elimination transition state with the more polar solvent.

The difference in the *E*:*Z* ratio of the 1-chloro-2-deuteroethylene products starting from either the *cis*-DCE or *trans*-DCE is puzzling and informative. From a Newman projection analysis, the same three rotomeric conformers are available starting from insertion of *cis*- or *trans*-DCE into a Rh–D bond (see Supporting Information). If bond rotation interconverting these rotomers is fast compared to elimination, this analysis suggests that *cis*- and *trans*-DCE should give the same ratio of products. We conclude that the converse must be true, that elimination is competitive with C–C bond rotation. The kinetic product mixture is observed, as the rotomers do not have time to fully equilibrate.⁷⁸

Occurrence of Hydrogenation/Hydrosilylation Products. Hydrogenation (1,2-addition) products are observed only in the H₂ catalytic system, providing further support for the involvement of a Rh(III)–H pathway with H₂. Hydrogenation products (dichloroethane, chloroethane, fluoroethane, chlorofluoroethane, and ethane) were observed during the degradation of various halogenated ethylenes with H₂ and (PPh₃)₃RhCl, supporting the involvement of a Rh(III)–alkyl complex in this catalytic system, as reductive elimination is not favorable from a Rh(I) center. Therefore, observation of hydrogenation products supports the assertion that hydrogenation occurs from a Rh(III) complex.

No 1,2-addition (hydrosilylation) products were observed during the degradation of halogenated ethylene when Et₃SiH was used as the reducing agent. Hydrosilylation products would arise from insertion of the alkene into the Rh–SiEt₃ bond followed by reductive elimination to form Et₄Si. By contrast, Braun et al. recently reported hydrosilylation products in the degradation of hexafluoropropene catalyzed by a triethylphosphine rhodium complex.⁵⁶

Vinyl Fluoride Products. Differences in the products observed when (PPh₃)₃RhCl reacts with vinyl fluoride in the presence of Et₃SiH and H₂ provide further support for different degradation pathways with the two reducing agents. When Et₃SiH, (PPh₃)₃RhCl, and vinyl fluoride were reacted, the major degradation product is ethylene. However, when vinyl fluoride is reacted with H₂ and (PPh₃)₃RhCl, the major degradation product was fluoroethane, and

(78) Another possibility is that conformer interconversion is fast but that the position of the conformer equilibrium is perturbed by the site of deuteration.

the minor degradation product was ethylene. With Et_3SiH , the active Rh(I)-H would favor $\beta\text{-F}$ -elimination, giving ethylene as the product (step A, Figure 7). With H_2 , the active Rh(III)-H allows for either $\beta\text{-F}$ -elimination (producing ethylene, step B, Figure 8) or reductive elimination (producing fluoroethane, step C, Figure 8) after the insertion of the vinyl fluoride into the Rh-H bond.

Other Mechanistic Observations. In the Et_3SiH system, all of the dichloroethylenes are degraded at a similar rate (Table 1), while in the H_2 system, *cis*-DCE is degraded more readily than *trans*-DCE and 1,1-DCE (Table 2). A possible explanation for this difference in reactivity is that in the H_2 system the active catalyst, Rh(III)-H , is more sterically crowded and more selective in terms of alkene association.

Conclusions

Catalytic dechlorination of chlorinated ethylenes by $(\text{PR}_3)_3\text{RhCl}$ occurs with Et_3SiH and H_2 as reducing agents. These are therefore effective catalytic systems for the degradation of an important class of environmental contaminants. Rhodium hydride complexes are the active intermediates for the degradation of the halogenated ethylenes studied. The use of both Et_3SiH and H_2 is consistent

with an insertion/ β -chloride elimination mechanism, but due to distinct differences in the two systems, it is proposed that a Rh(I) pathway is favored for Et_3SiH and a Rh(III) pathway is favored for H_2 . From the Rh(I) pathway both *syn*- and *anti*- β -halo-elimination can occur, and from the Rh(III) pathway, only *syn*- β -halo-elimination occurs. The difference in reactivity between Et_3SiH and H_2 leads to different stereochemistry of elimination products and different propensities for giving 1,2-addition products. Therefore, direct comparisons between H_2 and Et_3SiH in this system need to be considered carefully.

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Supporting Information Available: Newman projections of dichloroalkylrhodium complexes from *cis*- and *trans*-DCE, representative halogenated ethylene degradation plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.