Supporting Information for
Phosphinorhodium-catalyzed Dehalogenation of Chlorinated and Fluorinated Ethylenes: Distinct Mechanisms with Triethylsilane and Dihydrogen

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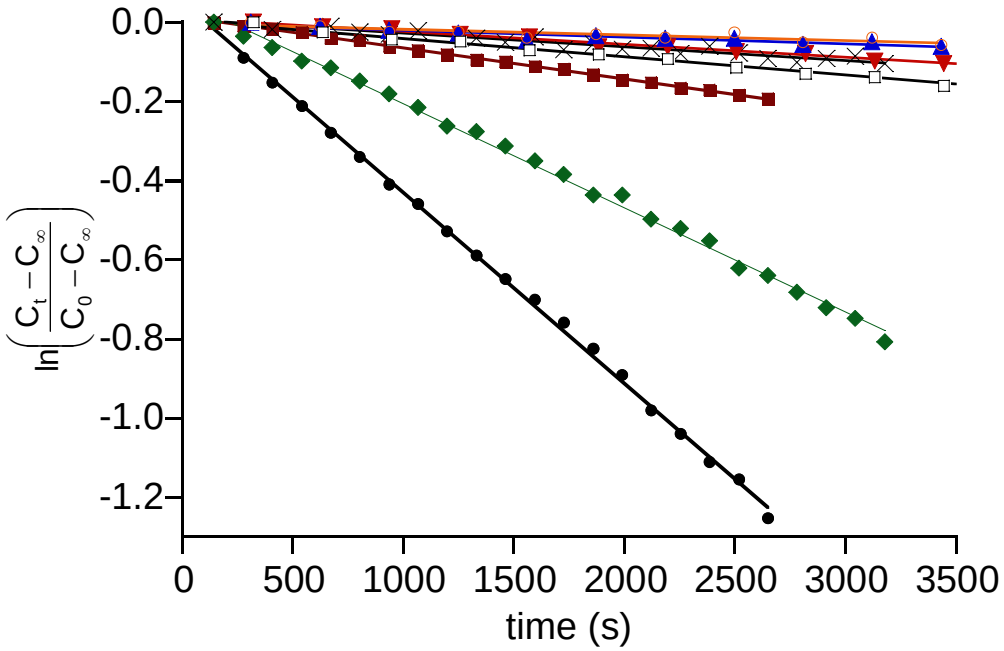

Figure S1. Representative linearized degradation of halogenated ethylene substrates versus time. Values were determined from loss of substrate using ^{1}H NMR at 35 °C. Each sealable NMR tube contained substrate (20-30 mM), catalyst ($(PPh_3)_3RhCl$, 2.4 mM), Et_3SiH (125 mM), and internal standard (*p*-xylene, 3.3 mM) in C_6D_6. Lines are linear fits to the experimental data. Vinyl fluoride (●); 1,1-fluorochloroethylene (♦); vinyl chloride (■); 1,1-dichloroethylene (□); 1,2-*cis*-dichloroethylene (▼); 1,2-*trans*-dichloroethylene (×); 1,2-*cis*-fluorochloroethylene (○); 1,2-*trans*-fluorochloroethylene (▲).

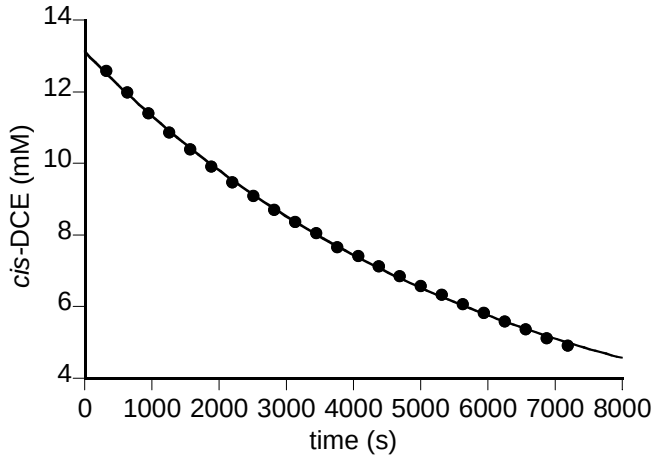

Figure S2. *cis*-DCE degradation by $(PPh_3)_3RhCl$ (2.4 mM) and Et_3SiH (125 mM) at 55 °C in the presence of 2.4 mM PPh_3. Concentrations of *cis*-DCE determined versus internal standard, *p*-xylene (3.3 mM). Fit is a nonlinear exponential first-order decay, $k_{obs} = 1.7 \times 10^{-4}\ s^{-1}$.

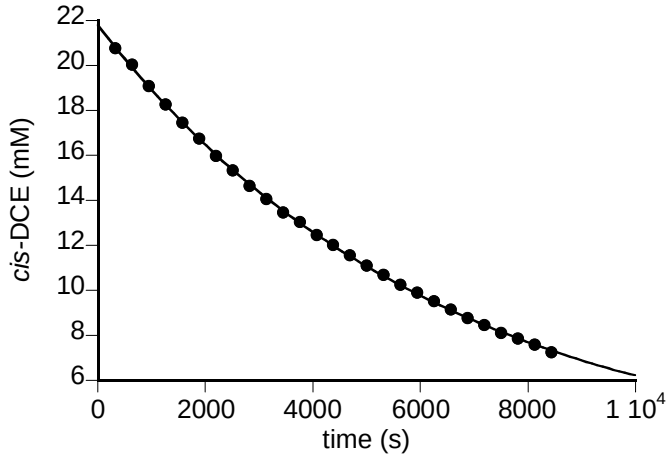

Figure S3. *cis*-DCE degradation by $(PPh_3)_3RhCl$ (2.4 mM) and Et_3SiH (125 mM) at 55 °C in the presence of 2.4 mM COD. Concentrations of *cis*-DCE determined versus internal standard, *p*-xylene (3.3 mM). Fit is a nonlinear exponential first-order decay, $k_{obs} = 1.6 \times 10^{-4}\ s^{-1}$.

Newman Projections depicting the three rotomers that result from insertion of *cis*-DCE (Figure S4) or *trans*-DCE (Figure S5) into a Rh-D to form a dichloroalkylrhodium. The three rotomers are the same for both DCEs (in blue) and are depicted in the same relative positions in the figures to illustrate this. The stereospecific products that would result from both *syn*- and *anti*-β-chloride elimination are also shown.

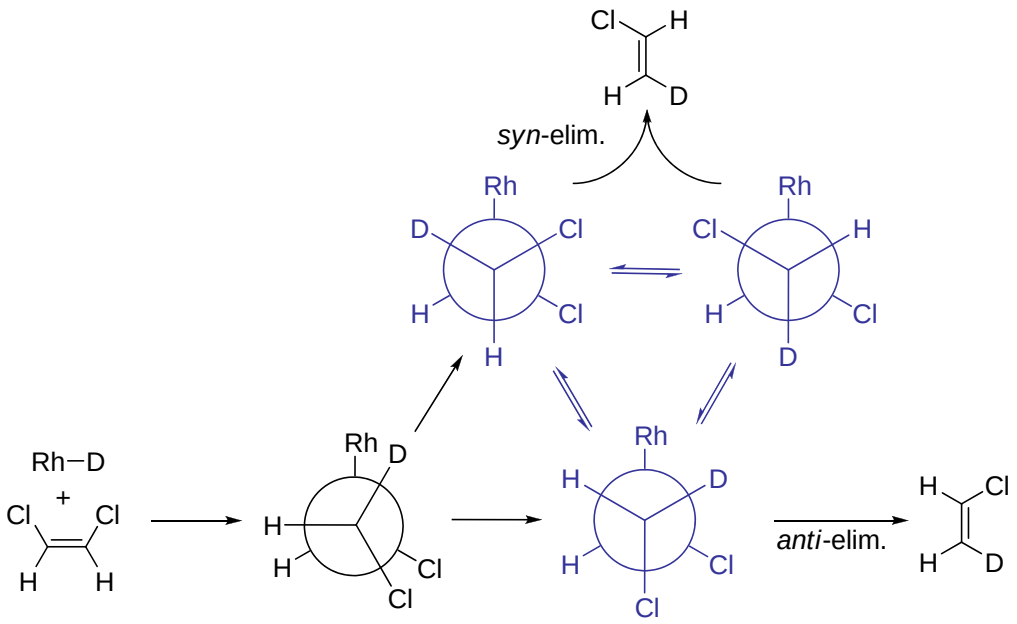

Figure S4. Newman projections for the three possible rotomers that result from insertion of *cis*-DCE into a Rh-D bond, as well as the stereospecific products that could come from each.

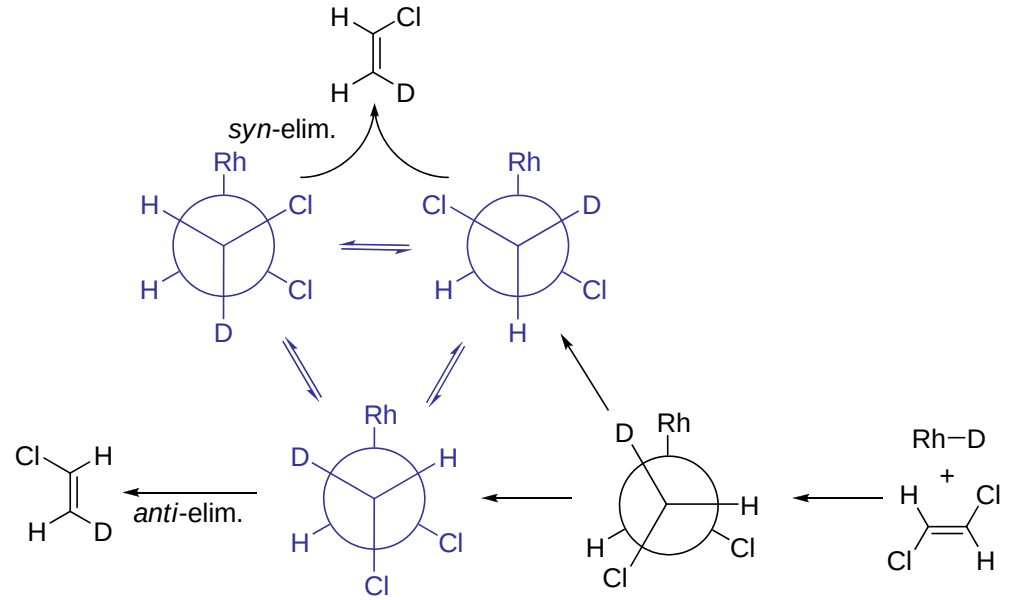

Figure S5. Newman projections for the three possible rotomers from insertion of *trans*-DCE into a Rh-D bond, as well as the stereospecific products that could come from each.