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FINAL REPORT

GRANT #: N00014-01-1-0583

PRINCIPAL INVESTIGATOR: Stephen G. DiMagno

INSTITUTION: University of Nebraska

GRANT TITLE: A Catalytic Reactor for Mechanistic Investigation of Hydrocarbon Functionalization

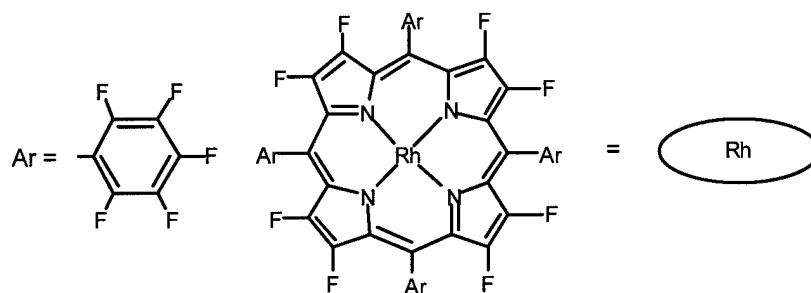
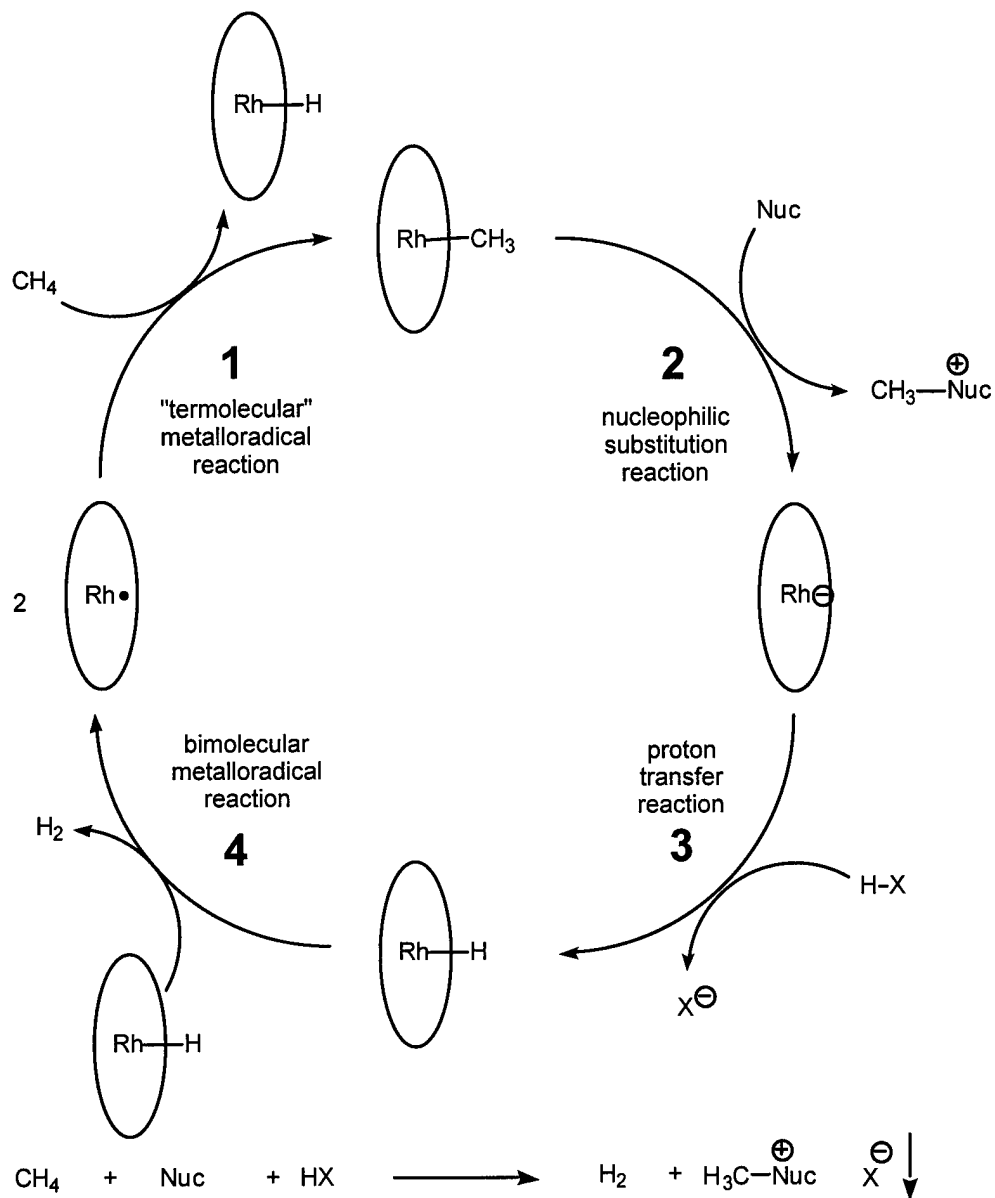
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OBJECTIVE: To construct a reactor that allows *in situ* monitoring and investigation of hydrocarbon functionalization under moderate pressure. This reactor supports research carried out under grant # N00014-00-1-0283.

APPROACH: Rhodium complexes of novel fluorinated porphyrins are prepared and their actions upon gaseous hydrocarbons, particularly methane, are followed by FT-IR spectroscopy and electrochemical analysis within the high-pressure reactor. The impact of varying ligand design, solvent, nucleophile, axial ligand, oxidant, and hydrocarbon or hydrogen pressures upon the rates and/or thermodynamics of the catalytic process are assessed similarly. In addition, extensive electrochemical studies of these catalysts in various solvent/electrolyte systems are performed to find systems compatible with direct electrochemical oxidation of the rhodium catalysts. The essential steps in this novel catalytic cycle are outlined in Scheme 1.

ACCOMPLISHMENTS: With the new pressure reactor, we performed kinetic studies of H₂ and D₂ activation and methane and deuteriomethane activation and evolution by Rh(F₂₈TPP) at moderate gas pressures and 293 °K, 313 °K, 333 °K, and 353 °K reaction temperatures. The rate constant for hydrogen activation was found to be nearly identical to that of Rh(TMP). Methane evolution was well fit by a second order kinetic model, indicating that the C-H activation reaction does involve two metalloradical centers in the rate determining step. Complementary H-D exchange

reactions with linear alkanes (heptane, decane) showed that C-H activation is selective toward 1° C-H bonds when both



Scheme 1. Methane functionalization cycle.

1° and 2° saturated carbon centers were present. These data indicate that the highly electrophilic nature of the metal center does not compromise the kinetics of the important homolytic bond-breaking steps in the cycle (reactions 1 and 4 in Scheme 1.)

Electrochemical Studies: We conducted a variety of electrochemical experiments aimed at determining what solvents, counterions, and potential nucleophiles were compatible with a stable rhodium metalloradical species. After extensive experimentation, it was found that the Rh(F₂₈TPP) metalloradical was stable in hydroxylic and/or nonpolar solvents containing weakly coordinating anions. Furthermore, aqueous mixtures of nonpolar solvents (saturated solutions) also supported a stable Rh(II) metalloradical. These results indicate that water or other hydroxylic nucleophiles are compatible with this catalytic process; this is a key finding given that alcohols are desirable end products.

CONCLUSIONS: Direct electrochemical oxidation of reduced Rh(F₂₈TPP) is possible under catalytic conditions. The kinetics of hydrocarbon functionalization indicate the alkane activation is rate limiting for the Rh(F₂₈TPP) catalyzed process.

SIGNIFICANCE: The reactor has allowed us to define the conditions permitting direct electrochemical oxidation of the reduced form of the catalyst. This key finding should enable a greater breadth of nucleophiles, including oxygen nucleophiles, to be used in hydrocarbon functionalization reactions catalyzed by rhodium porphyrins.

PUBLICATIONS AND ABSTRACTS:

1. Wertsching, A. K., Koch, A. S., and DiMagno, S. G., (2001), "On the Negligible Impact of Ruffling on the Electronic Spectra of Porphine, Tetramethylporphyrin, and Perfluoroalkylporphyrins", *J. Am. Chem. Soc.* **2001**, *123*, 3932-3939.
2. Smirnov, V. V., Woller, E. K., Tatman, D. and DiMagno S. G., (2001), "Structure and Photophysics of β -Octafluoro-meso-tetraarylporphyrins", *Inorg. Chem.* **2001**, *40*, 2614-2619.

3. DiMugno, S. G.; Sun, H.; Nelson, A. P. (2001)
"Hydrocarbon Activation and Conversion by Electrophilic Rhodium Porphyrin Complexes", Abstracts of Papers, 222nd ACS National Meeting, Chicago, IL, United States, August 26-30, 2001.
 4. DiMugno, S. G.; Biffinger, J. C.; Sun, H. "Reactivity of Iridium and Rhodium Thiaporphyrins", (2001) Abstracts of Papers, 222nd ACS National Meeting, Chicago, IL, United States, August 26-30, 2001.
 5. DiMugno, S. G.; Smirnov, V. V. "Organometallic Complexes of Electron-deficient Zirconium(IV) Porphyrins. (2001) Abstracts of Papers, 222nd ACS National Meeting, Chicago, IL, United States, August 26-30, 2001.
 6. DiMugno, S. G.; Sun, H.; Biffinger, J.; Nelson, A. P. "Electrochemistry of a Series of Rhodium Porphyrins: New Understanding of the Relationship between Electrochemical Properties and Coordination Properties of the Rhodium Porphyrins", (2002) Abstracts of Papers, 223rd ACS National Meeting, Orlando, FL, United States, April 7-11, 2002.
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