HYDROGEN SPLITTING COMPOSITION

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority benefit of U.S. Provisional Applications 60/865,684 filed November 14, 2006; and 60/896,557 filed March 23, 2007 the contents of which are hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention in general relates to compounds and compositions capable of splitting dihydrogen, and in particular to compounds and compositions dissociating dihydrogen and use of said compounds in metal-free hydrogenation. These species are also capable of transfer hydrogenation.

BACKGROUND OF THE INVENTION

[0003] The generation and use of molecular hydrogen (H_2) are important processes to fundamental chemical transformations and biological functions. The overwhelming majority of systems known to either liberate or react with H_2 involve reaction at a transition metal center. Hydrogenase enzymes, as well as a plethora of synthetic stoichiometric and catalytic reagents for hydrogenation reactions, are based on the processes of oxidative addition and reductive elimination of H_2 at a metal center. Metal-free systems that either react with or liberate H_2 are rare. A unique metal-free hydrogenase from *methanogenic archaea*s has been shown to catalyze reactions with H_2, and theoretical studies suggest the role of a folate-like cofactor in the reversible activation/liberation of H_2. Several metal-free systems have been shown to activate H_2. For example, main group element-H_2 reactions in low temperature matrices are also known.

[0004] Hydrogenation is the addition of hydrogen to unsaturated organic compounds. Such reactions are used for the production of a myriad of chemical products worldwide, from large-scale operations including the upgrading of crude oil and the production of bulk commodity materials to the synthesis of a variety of fine chemicals used in the food, agricultural, and pharmaceutical industries. The process of hydrogen addition to unsaturated precursors is mediated by either homogeneous or heterogeneous transition metal based catalysts. In the 1960s, the advent of organometallic chemistry gave rise to homogeneous transition metal based hydrogenation catalysts for a variety of substrates. The operation of these catalysts hinges on the key step of oxidative addition of hydrogen. More recently, transition metal systems that effect heterolytic cleavage of hydrogen at a metal center have been uncovered. In these cases, a metal hydride is formed with concurrent protonation of an amido ligand.

[0005] Non-transition metal catalysts for hydrogenation reactions are all but unknown. KO*t*Bu has been shown to act as a catalyst effecting the addition of H_2 to benzophenone under forcing conditions of 200°C and greater than 100 bar H_2. Organocatalysts have been developed for hydrogenations of enones and imines; however, such systems do not employ H_2 directly but rather a surrogate such as a Hantzsch ester as the stoichiometric source of hydrogen. The development of nonmetal hydrogenation catalysts hinges on the discovery of systems that react cleanly with H_2, but few are known. Power and coworkers reported the hydrogenation of Ge_2–alkyne analogues to give a mixture of Ge_2 and primary germane products. J. W. Yang, M. T. Hechavarria Fonseca, B. List, Angew. Chem. 2004, 116, 6829; Angew. Chem. Int. Ed. 2004, 43, 6660. G. H. Spikes, J. C. Fettinger, P. P. Power, J. Am. Chem. Soc. 2005, 127, 12 232. It should be noted that non-transition metal systems have been shown to effect hydrogenation under more forcing conditions. For example, DeWitt, Ramp and Trapasso demonstrated hydrogenation with

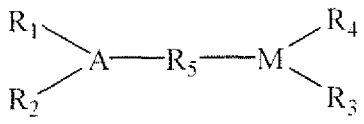
iPr_3B under 67 atm (1000psi) H_2 at 220°C. E. J. DeWitt, F. L. Ramp, L. E. Trapasso, *J. Am. Chem . Soc.* **1961**, *83*, 4672-4672; F. L. Ramp, E. J. DeWitt, L. E. Trapasso, *Org. Chem.*, **1962**, *27*, 4368-4372). Similarly, Haenel and coworkers (E. Osthaus, M. W. Haenel, in Coal Science and Technology, Vol. 11 Elsevier, Amsterdam, 1987, pp. 765-768 (Proc. 1987 Intern. Conf. Coal Sci., Eds.: J. A. Moulijn, K. A. Nater, H. A. G. Chermin),; M. Yalpani, R. Köster, M. W. Haenel, Erdoel Kohle, Erdgas, *Petrochem.* **1990**, *43*, 344-347; M. W. Haenel, J. Narangerel, U.-B. Richter, A. Rufinska, *Angew. Chem.* **2006**, *118*, 1077-1082; *Angew. Chem. Int. Ed.* **2006**, *45*, 1061-1066; M. W. Haenel, J. Narangerel, U.-B. Richter, A. Rufinska, *Prep. Pap. Am. Chem. Soc., Div. Fuel Chem.* **2006**, *51(2)*, 741-742) among others showed hydrogenation of coal under almost 15 MPa and 280-350°C using BI_3 or alkyl boranes. M. Yalpani, T. Lunow, R. Köster, *Chem. Ber.* **1989**, *122*, 687-693; (b) M. Yalpani, R. Köster, *Chem. Ber.* **1990**, *123*, 719-724. As well, superacid systems have also been shown to effect hydrogenation of alkenes using H_2 pressures of at least 35 atm. M. Siskin, *J. Am. Chem. Soc.* **1974**, *96*, 3641; (b) J. Wristers, *J. Am. Chem. Soc.* **1975**, *97*, 4312.

[0006] The ability to dissociate dihydrogen represents a reaction of considerable importance in fields including hydrogenation of ethenically unsaturated feed stocks, chemical fuel storage, hydrogen purification, and hydrogen getters that prevent hydrogen levels from building beyond a preselected threshold. Traditionally, dihydrogen dissociation has involved the use of metal catalysts and in particular palladium. Conventional catalysts inclusive of metal have a number of limitations that include high material cost, high density, the heterogeneous nature of such catalysts relative to liquid phase reactants, and contamination of resultant products with metal catalysts.

[0007] Thus, there exists a need for a hydrogen dissociation catalyst that is independent of metal. Additionally, a catalyst capable of operating as a homogeneous catalyst would afford considerable operational advantages. Further, these hydrogen catalysts operate efficiently at lower or comparable temperatures to those used for existing metal based hydrogenation catalysts.

SUMMARY OF THE INVENTION

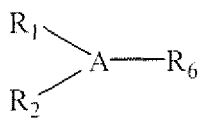
[0008] A compound is provided that is operative as a hydrogenation catalyst. The compound is capable of homogenous liquid phase catalysis exclusive of a noble metal. A compound has the formula:



I

where each of R_1, R_2, R_3 and R_4 is independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_{16}-C_{30} linear alkyl-, RO-, -NRR', -PRR', -SR, fluoro substituted forms thereof, and perfluoro forms thereof; and R_5 is C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_3-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, RO-, -NRR', -PRR', -SR, fluoro substituted forms thereof, and perfluoro forms thereof; where R and R' are each independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; A is N, P, S, or O with the proviso that when A is S or O, R_2 is a nullity; and M is B, Al, Ga or In.

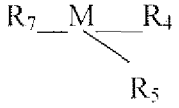
[0009] A composition operative as a hydrogenation catalyst includes a compound having the formula:



II

where each of R_1 and R_2 is independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_{16}-C_{30} linear alkyl-, RO-, -NRR', -PRR', -SR, fluoro substituted forms thereof, and perfluoro forms thereof; R_6 is C_1-C_{30} alkyl-, C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, RO-, -NRR', -PRR', -SR, a fluoro substituted form thereof, a perfluoro substituted form thereof, H or F; where R and R' are each independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; A is N, P, S, or O with the proviso that when A is S or O, R_2 is a nullity;

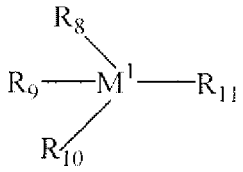
in fluid communication with a composition having the formula:



III

where each of R_4, R_5 and R_7 is independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_{16}-C_{30} linear alkyl-, RO-, -NRR', -PRR', -SR, fluoro substituted forms thereof, and perfluoro forms thereof; where R and R' are each independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8

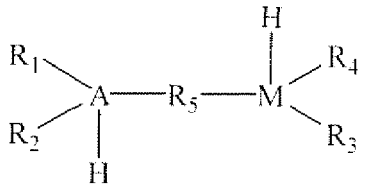
cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; and M is B, Al, Ga or In; or a composition of the formula:



V

where M^1 is Ti, Zr or Hf; each of R_8, R_9 and R_{10} is independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, amide, alkoxide, phenoxide, phosphinimide, cyclopentadienyl, indenyl, fluorenyl derivatives, RO-, -NRR', -PRR', -SR, fluoro substituted forms thereof, and perfluoro forms thereof; where R and R' are each independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; and R_{11} is C_1-C_{20} alkyl linear or branched with the proviso that R_{11} is a better leaving group than any of R_8, R_9 or R_{10} under nucleophic attack by a hydrogen or other alkyl abstracting agents to yield a cationic M^1 species.

[0010] A compound is also provided that is an addition reaction product of a compound of formula I and dihydrogen (H_2). The compound has the formula:



IV

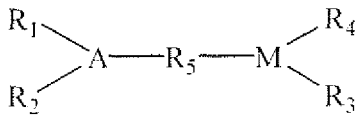
where each of R_1, R_2, R_3 and R_4 is independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_{16}-C_{30} linear alkyl-, RO-, -NRR`, -PRR`, -SR, fluoro substituted forms thereof, and perfluoro forms thereof; and R_5 is C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_3-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; where R and R` are each independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; A is N, P, S, or O with the proviso that when A is S, R_2 is a nullity; and M is B, Al, Ga or In.

[0011] A process of catalytic hydrogenation of a substrate comprising: independently compound I, a mixture of II and III, compound III, a mixture of II, III-V, compound IV, or compound VI together with dihydrogen and solvent form a catalyst whereby hydrogenation of a substrate is effected.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0012] The present invention has utility as compounds and compositions capable of dissociating dihydrogen and reversibly binding hydrogen atoms. In addition to dihydrogen dissociation, a sacrificial dihydrogen source such as primary or secondary amines, primary or secondary phosphines, alcohols and thiols are also is operative according to the present invention to reduce substrates. According to the present invention, a compound is provided that is the reaction product of a sterically hindered Lewis acid with a sterically hindered Lewis base via an

intermediate linker group therebetween. The prototypical form of an inventive compound I is a reaction product of linker separated sterically hindered phosphine and a sterically hindered borane. An inventive compound has the formula:

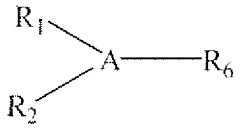


I

where each of R_1, R_2, R_3 and R_4 is independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_{16}-C_{30} linear alkyl-, RO-, -NRR', -PRR', -SR, fluoro substituted forms thereof, and perfluoro forms thereof; and R_5 is C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_3-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, RO-, -NRR', -PRR', -SR, fluoro substituted forms thereof, and perfluoro forms thereof; where R and R' are each independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; A is N, P, S, or O with the proviso that when A is S or O, R_2 is a nullity; and M is B, Al, Ga or In.

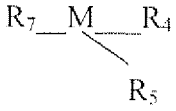
[0013] A bimolecular composition according to the present invention capable of dissociating hydrogen and reversibly binding hydrogen atoms includes in a mixture of a phosphine and a borane incapable of reaction owing to steric hindrance. Sterically hindered phosphine is readily replaced with a nitrogen, oxygen, or sulfur analog as shown in formula II. Sterically hindered borane is readily replaced with an aluminum, gallium, or indium analog as shown in formula III. Lesser sterically hindered systems exhibit reactivity at temperatures

dependent on the nature of the compounds. The mixture of sterically hindered Lewis base and Lewis compounds operative herein have the formulae II and III, respectively:



II

where each of R_1 and R_2 is independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_{16}-C_{30} linear alkyl-, RO-, -NRR', -PRR', -SR, fluoro substituted forms thereof, and perfluoro forms thereof; R_6 is C_1-C_{30} alkyl-, C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, RO-, -NRR', -PRR', -SR, a fluoro substituted form thereof, a perfluoro substituted form thereof, H or F; where R and R' are each independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; A is N, P, S, or O with the proviso that when A is S or O, R_2 is a nullity.

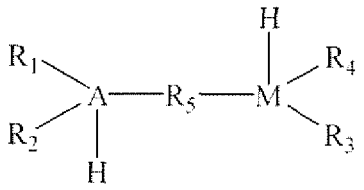


III

where each of R_4, R_5 and R_7 is independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_{16}-C_{30} linear alkyl-, RO-, -NRR', -PRR', -SR, fluoro substituted forms thereof, and perfluoro forms thereof; where R and R' are each independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8

cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; and M is B, Al, Ga or In. In a particular embodiment a sterically hindered perfluorinated composition of formula III has hydrogen catalytic activity independent of the presence of a compound of formula II.

[0014] A compound of the formula is also provided that is reversibly converted into the compound of formula I through loss of two hydrogen atoms. The compound has the formula:

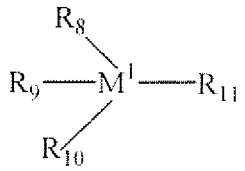


IV

where each of R_1, R_2, R_3 and R_4 is independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_{16}-C_{30} linear alkyl-, RO-, -NRR', -PRR', -SR, fluoro substituted forms thereof, and perfluoro forms thereof; and R_5 is C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_3-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; where R and R' are each independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; A is N, P, S, or O with the proviso that when A is S, R_2 is a nullity; and M is B, Al, Ga or In.

[0015] In an alternate embodiment, hydrogenation occurs through the interaction of a composition of formula II with a transition metal cation of Ti, Zr, or Hf when A is P or N. The

transition metal cation is generated *in situ* by alkyl group abstraction from an organometallic composition of the formula:



V

where M^1 is Ti, Zr or Hf; each of R_8, R_9 and R_{10} is independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, amide, alkoxide, phenoxide, phosphinimide, cyclopentadienyl, indenyl, fluorenyl derivatives, RO-, -NRR', -PRR', -SR, fluoro substituted forms thereof, and perfluoro forms thereof; where R and R' are each independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; and R_{11} is C_1-C_{20} alkyl linear or branched with the proviso that R_{11} is a better leaving group than any of R_8, R_9 or R_{10} under nucleophic attack by a hydrogen or other alkyl abstracting agents to yield a cationic M^1 species.

[0016] The present invention compounds and mixtures of compounds are effective as hydrogenation catalysts for performing reactions illustratively including those provided in Table 1. The compositions and compounds of formulae I-V are operative in hydrogenation catalysis in a neat liquid substrate, in a solution containing substrate, or applied as coating on an inert support.

Table 1. Substrate hydrogenation to products according to the present invention.

Substrates	Products
ketimines	amines
ketene-imines	amines
aldimines	amines
nitriles	amines
aziridines	amines
olefins	hydrocarbon
ketones	alcohols
aldehydes	alcohols
borazines	borane-amine adducts
acetylene	hydrocarbon
enols	alcohols
enamines	amines
ketenes	alcohol
allenes	alkanes
esters	alcohols
epoxides	alcohols
isocyanides	amines
lactones	diols

[0017] The present invention is further detailed with respect to the following nonlimiting examples.

Example 1 – General Catalysis Procedure.

[0018] The catalyst (0.1-20 mol %) is weighed into a 50 ml round bottomed Schlenk flask and slurried in toluene (2 ml). The reaction is charged with H_2. The slurry is then allowed to equilibrate at the desired temperature under an atmosphere of H_2 with rapid stirring. A solution of substrate (1.0 mmol) in toluene (2 ml) is added via syringe. Reaction time and temperature vary with substrate. In all cases, the crude mixtures of the completed reactions are pure to the limits of NMR spectroscopy. The product is purified by all volatiles being removed *in vacuo* trap to trap vacuum distillation or filtration through a small plug of silica to remove residual catalyst.

Example 2 – Conversion of *N*-benzylidine-*tert*-butyl amine to benzyl-*tert*-butylamine with tBu$_2$PH-C$_6$F$_4$-BH(C$_6$F$_5$)$_2$.

[0019] In a glove box, tBu$_2$PH-C$_6$F$_4$-BH(C$_6$F$_5$)$_2$ (0.033 g, 0.05 mmol) is weighed into a 50 ml round bottomed Schlenk flask equipped with a small stir bar and slurried in toluene (2 ml). The reaction is attached to a vacuum/H_2 line and freeze-pump-thaw cycled three times. The slurry is then allowed to equilibrate at 80°C under an atmosphere of H_2 with rapid (500 rpm) stirring. A solution of *N*-benzylidine-*tert*-butyl amine (0.161 g, 1.0 mmol) in toluene (2 ml) is added via syringe. The reaction is periodically monitored by thin layer chromatography (silica, eluent: 1:5 ethyl acetate/hexanes) and ^{1}H NMR spectroscopy and is complete in 1 hour. The solvent is removed *in vacuo* and the product benzyl-*tert*-butylamine is purified by trap to trap vacuum distillation. Isolated yield 0.128 g (79%).

Example 3 – Alternate General Catalysis Procedure.

[0020] The catalyst (0.01 – 0.20 mmol) and substrate (1 mmol) are weighed into a 100 ml round bottomed glass flask equipped with a Kontes valve. Solvent (4 ml) is added, the reaction transferred to a vacuum/H_2 line and the mixture is freeze-pump-thaw cycled three times. The mixture is cooled to -196°C (liquid N_2) and 1 atm. H_2 is introduced. The flask is sealed, the reaction is placed in a preheated bath and rapidly stirred. Reaction time and temperature vary with substrate. In all cases, the crude reaction mixtures are of the completed reactions are pure to the limits of NMR spectroscopy. The product is purified by removal of all volatiles *in vacuo* and trap to trap vacuum distillation or filtration through a small plug of silica to remove residual catalyst.

Example 4 – Conversion of *cis*-1,2,3-triphenylaziridine to *N*-1,2 diphenylethyl-*N*-phenyl amine with tBu$_2$PH(C$_6$F$_4$)BH(C$_6$F$_5$)$_2$.

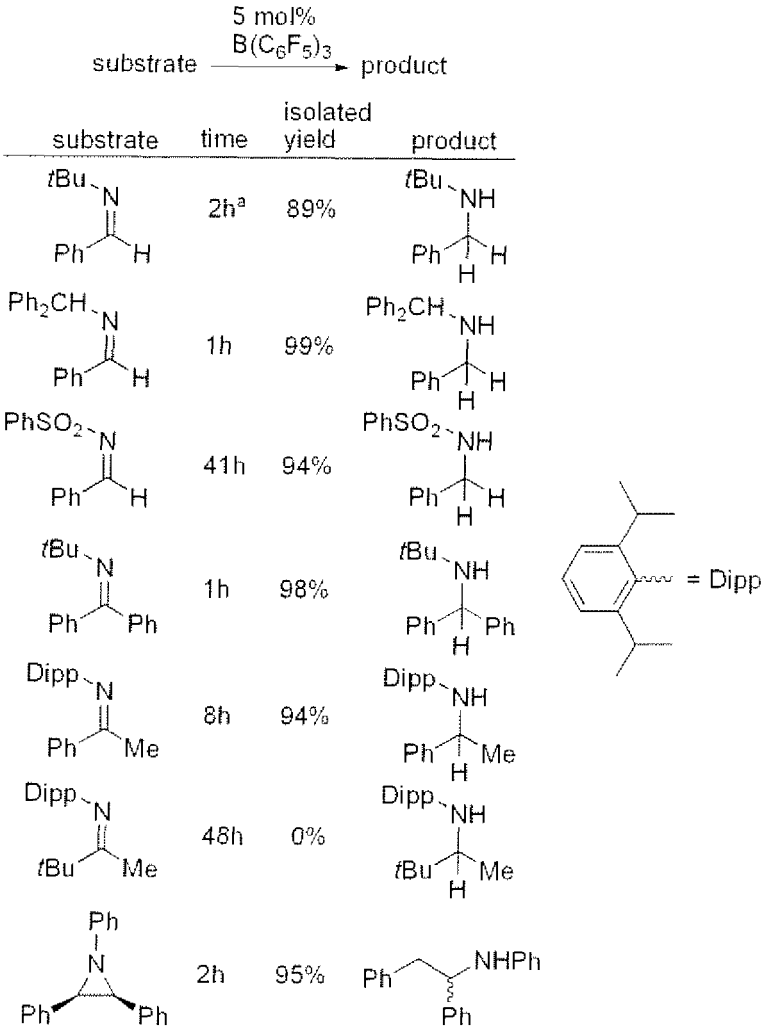
[0021] In a glove box, tBu$_2$PH(C$_6$F$_4$)BH(C$_6$F$_5$)$_2$ (0.33 g, 0.05 mmol) and *cis*-1,2,3-triphenylaziridine (0.271 g, 1.0 mmol) were weighed into a 100 ml round bottomed glass flask equipped with a Kontes valve and a magnetic stirbar. Toluene (4 ml) is added, the reaction transferred to a vacuum/H_2 line and the mixture is freeze-pump-thaw cycled three times. The mixture is cooled to -196°C (liquid N_2) and 1 atm. H_2 is introduced. The flask is sealed, the reaction is placed in a 120°C preheated bath and rapidly (500 rpm) stirred. The reaction is periodically monitored by ^{1}H NMR spectroscopy and is complete in 2 hours. The reaction mixture is poured onto a small plug of silica and eluted with 2:1 hexanes/ethyl acetate (50 ml). The solvent is removed *in vacuo* and the product *N*-1,2-diphenylethyl-*N*-phenyl amine isolated. Yield: 0.269 g (98%)

Comparative Example – B(C$_6$F$_5$)$_3$-only Reductive Catalysis.

[0022] In the glovebox, a substrate (1 mmol) per Table 2, B(C$_6$F$_5$)$_3$ (26 mg, 0.05 mmol, 5 mol%) and dry toluene (4 ml) are weighed into a 100 ml round bottomed flask equipped with a sealable Teflon tap and small magnetic stirbar. The reaction is then attached to a double manifold H_2/vacuum line and degassed (freeze-pump-thaw cycle x 3). The reaction is cooled to -196°C (liquid N_2) and 1 atm. H_2 is introduced. The flask is sealed and warmed to room temperature. The reaction is then placed in an oil bath heated to the desired temperature and stirred at 500 rpm. At 120°C, the H_2 pressure is ~ 5 atm. Aliquots are obtained at periodic intervals by rapidly cooling the reaction in a water bath and venting the H_2 pressure. Samples are taken by pipette in the glove box. The reaction is re-pressurized using the above procedure. Upon full conversion, the reaction is poured onto a 10 cm plug of silica (200 mesh) and eluted with 2:1 hexanes/ethyl acetate (200 ml). If the amine is not fully soluble in the reaction mixture

or the hexanes/ethyl acetate solvent, CH_2Cl_2 (3 x 5 ml) is used to wash the reaction vessel. The collected solvent is removed *in vacuo* to obtain the product in the time and yield shown in Table 2.

Table 2. $B(C_6F_5)_3$-only catalyzed reductions. Conditions: 120°C, toluene, ~ 5 atm. H_2, 500 rpm stir rate.



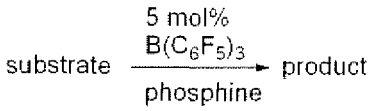
a: conditions, 1 atm. H_2, 80°C

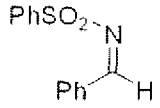
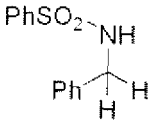
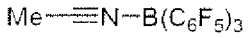
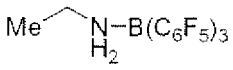
Example 5 – $B(C_6F_5)_3$ and Phosphine Reductive Catalysis.

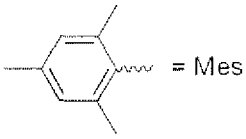
[0023] In the glovebox, a substrate (1 mmol) per Table 3, is reacted in the presence of $P(2,4,6\text{-}Me_3C_6H_2)_3$ (19 mg 0.05 mmol, 5 mol%) or $PtBu_3$, (10 mg, 0.05 mmol, 5 mol%)

according to the procedure of the Comparative Example. As shown in Table 3, more efficient reaction with the sterically hindered phosphine (formula II) is noted for the imine $PhCH(N)SO_2Ph$ and $MeCN–B(C_6F_5)_3$ reacts when no reductive catalysis is noted absent the phosphine (formula II).

Table 3. Comparison of $B(C_6F_5)_3$-only and $B(C_6F_5)_3/PMes_3$ catalyzed reductions. Conditions: 120°C, toluene, ~ 5 atm. H_2, 500 rpm stir rate.



substrate	phosphine (mol%)	time	isolated yield	product
	-	41h	94%	
	$PMes_3$ (5)	8h	98%	
	-	48h	0%	
	$PMes_3$ (5)	49h	91%	



Example 6 – Imine and Nitrile Reduction.

[0024] In a glove box, a 100 mL glass bomb equipped with a small stir bar and a Teflon screw tap is charged with imine (1 mmol), catalyst (0.05 mmol, 5 mol%), and dry toluene (4 mL). The reaction is transferred to the vacuum/H_2 line and is degassed three times with a freeze–pump–thaw cycle. The reaction flask is cooled to -196°C, 1 atm of H_2 is introduced, and the flask then sealed and warmed to room temperature. The reaction is placed in a preheated oil bath and stirred at 500 rpm; at 120°C, this gave an H_2 pressure of about 5 atm. To take aliquots, the reaction is cooled rapidly in an ice bath, vented to release the H_2 pressure, and taken into a glove box. For the catalyst $(2,4,6\text{-}Me_3C_6H_2)_2\ PH(C_6H_4)\ BH(C_6F_5)_2$ (denoted as compound 1) and $(tert\text{-}butyl)_2\ PH(C_6H_4)\ BH(C_6F_5)_2$ (denoted as compound 2), the following products are obtained in the time and yield shown in Table 4.

Table 4. Imine and nitrile reduction by catalyst compositions 1 and 2.

Entry	Substrate	Catalyst	T	[8C]	t [h]	Yield [%]	Product
1	Ph(H)C=NtBu	1[b]		80	1	79	$PhCH_2NHtBu$
2	Ph(H)C=NtBu	2[b]		80	1	98	$PhCH_2NHtBu$
3	Ph(H)C=NSO_2Ph	1		120	10.5	97	$PhCH_2NHSO_2Ph$
4	Ph(H)C=NSO_2Ph	2		120	16	87	$PhCH_2NHSO_2Ph$
5	Ph(H)C=$NCHPh_2$	1		140	1	88	$PhPhCH_2NHCHPh_2$
6	Ph(H)C=NCH_2Ph	1		120	48	5[c]	$PhCH_2NHCH_2Ph$
7	Ph(H)C=$NCH_2Ph(B(C_6F_5)_3)$	1		120	46	57	$PhCH_2NHCH_2Ph(B(C_6F_5)_3)$
8	$MeCNB(C_6F_5)_3$	1		120	24	75	$MeCH_2NH_2B(C_6F_5)_3$
9	$PhCNB(C_6F_5)_3$	1		120	24	84	$PhCH_2NH_2B(C_6F_5)_3$
10	$(CH_2CH_2CNB(C_6F_5)_3)_2$	1[d]		120	48	99	$(CH_2CH_2CH_2NH_2B(C_6F_5)_3)_2$
11	PhCHCHPhNPh	1[d]		120	1.5	98	$PhCH_2CHPhNHPh$

[a] Standard conditions: 5 mol % catalyst, 4 mL toluene, ca. 5 atm H_2. [b] 1 atm H_2. [c] Determined by 1H NMR spectroscopy. [d] 10 mol % catalyst.

Example 7 – Synthesis of $[R_3P(C_6F_4)BF(C_6F_5)_2]$ R = isopropyl (denoted as compound 2), R = cyclohexyl (denoted as compound 4), of $[R_2PH(C_6F_4)BF(C_6F_5)_2]$ R = tert-butyl (denoted as compound 5) and $(2,4,6\text{-}Me_3C_6H_2)_3$ (denoted as compound 6).

[0025] These compounds are prepared in a similar fashion. A clear yellow solution of $B(C_6F_5)_3$ (0.500 g, 0.98 mmol) and *i*-Pr_3P (0.156 g, 0.98 mmol) or molar equivalent of $(C_6H_{11})_3P$, $(t\text{-}Bu)_3P$, or $(2,4,6\text{-}Me_3C_6H_2)_3P$ in toluene (20 mL) is allowed to stir for 12 h at 25°C during which time a white precipitate formed. Pentane (10 mL) is added, the mixture filtered and dried *in vacuo* for 1 h. In the instance of $(2,4,6\text{-}Me_3C_6H_2)_3P$ stirring took place in refluxing toluene. The product is collected as a white solid.

Example 8 – Synthesis of $[R_3P(C_6F_4)BH(C_6F_5)_2]$ R = isopropyl (denoted as compound 7), R = cyclohexyl (denoted as compound 8), of $[R_2PH(C_6F_4)BH(C_6F_5)_2]$ R = *t*-Bu (denoted as compound 9), and $(2,4,6\text{-}Me_3C_6H_2)_3$ (denoted as compound 10).

[0026] To a solution of compound 3 (0.400 g, 0.600 mmol) or a molar equivalent of compounds 4, 5 or 6 dissolved in CH_2Cl_2 (10 mL) is added $(CH_3)_2SiHCl$ (0.66 mL, 6.00 mmol) via syringe. The reaction is allowed to stir 12 h, during which time a precipitate forms. All volatiles are removed *in vacuo* to give the product as a white solid.

Example 9 – Synthesis of $[R_3P(C_6F_4)B(C_6F_5)_2][B(C_6F_5)_4]$ R = isopropyl (denoted as compound 11), R = cyclohexyl (denoted as compound 12), of $[R_2PH(C_6F_4)B(C_6F_5)_2][B(C_6F_5)_4]$ R = *t*-Bu (denoted as compound 13), ($2,4,6\text{-}Me_3C_6H_2$) (denoted as compound 14).

[0027] An orange solution of $[Ph_3C][B(C_6F_5)_4]$ (0.420 g, 0.456 mmol) in CH_2Cl_2 (2 mL) is added to a slurry of compound 7 (0.300 g, 0.457 mmol) or molar equivalent of 8, 9, or 10 in CH_2Cl_2 (5 mL) to give a faint yellow solution. The reaction is allowed to stir for 30 min and the volatiles are removed *in vacuo*. Pentane (5 mL) is added and the mixture filtered and washed with toluene (2 mL) and pentane (3 x 2 mL) to give an off white solid.

Example 10 – Synthesis of $R_2P(C_6F_4)B(C_6F_5)_2$ R = tert-butyl (denoted as compound 15), ($2,4,6\text{-}Me_3C_6H_2$) (denoted as compound 16).

[0028] A 20 mL vial is charged with compound 5 (0.099 g, 0.150 mmol) or a molar equivalent of composition 6, toluene (10 mL) and diethyl ether (1 mL), forming a white slurry. The mixture is cooled to -35°C and 3.0 M MeMgBr in diethyl ether (0.060 mL, 0.180 mmol) is added via syringe. Immediate formation of a clear yellow solution is observed. The reaction is allowed to warm to room temperature and stirred for 12 h. All volatiles are removed *in vacuo* and the product extracted with hexanes (3 x 5 mL) and filtered through celite. The solvent is removed *in vacuo* to give a yellow solid.

Example 13 – Conversion of *cis*-1,2,3-triphenylaziridine to *N*-1,2-diphenylethyl-*N*-phenyl amine with B(C6F5)3 and ($2,4,6\text{-}Me_3C_6H_2)_3P$.

[0029] In a glovebox, *cis*-1,2,3-triphenylaziridine (1 mmol), $B(C_6F_5)_3$ (6.05 mmol) and $(2,4,6\text{-}Me_3C_6H_2)_3P$ (0.05 mmol) are reacted according to the procedure of the Comparative Example to yield *N*-1,2-diphenylethyl-*N*-phenyl amine.

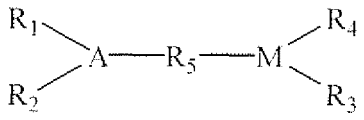
[0030] Patent documents and publications mentioned in the specification are indicative of the levels of those skilled in the art to which the invention pertains. These documents and

publications are incorporated herein by reference to the same extent as if each individual document or publication was specifically and individually incorporated herein by reference.

[0031] The foregoing description is illustrative of particular embodiments of the invention, but is not meant to be a limitation upon the practice thereof. The following claims, including all equivalents thereof, are intended to define the scope of the invention.

CLAIMS

1. A compound having the formula:



1

where each of R_1, R_2, R_3 and R_4 is independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_{16}-C_{30} linear alkyl-, RO-, -NRR', -PRR', -SR, fluoro substituted forms thereof, and perfluoro forms thereof; and R_5 is C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_3-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, RO-, -NRR', -PRR', -SR, fluoro substituted forms thereof, and perfluoro forms thereof; where R and R' are each independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; A is N, P, S, or O with the proviso that when A is S or O, R_2 is a nullity; and M is B, Al, Ga or In.

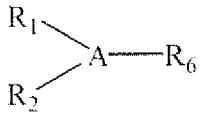
2. The compound of claim 1 wherein A is P and M is B.

3. The compound of claim 1 or 2 wherein R_3 and R_4 are identical perfluorinated groups and R_5 is perfluorinated.

4. The compound of claim 2 wherein R_1-R_5 are all one of C_6-C_{18} aryl, C_6-C_{18} having perfluorinated C_6-C_{18} aryl.

5. The compound of claim 2 wherein R_1 and R_2 are both 2,4,6-$(CH_3)_3$ C_6H_2.

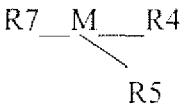
6. A composition comprising a compound having the formula:



II

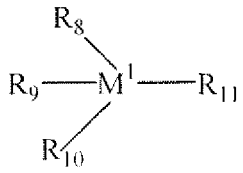
where each of R_1 and R_2 is independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_{16}-C_{30} linear alkyl-, RO-, -NRR', -PRR', -SR, fluoro substituted forms thereof, and perfluoro forms thereof; R_6 is C_1-C_{30} alkyl-, C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, RO-, -NRR', -PRR', -SR, a fluoro substituted form thereof, a perfluoro substituted form thereof, H or F; where R and R' are each independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; A is N, P, S, or O with the proviso that when A is S or O, R_2 is a nullity; in fluid communication with a composition

having the formula:



III

where each of R_4, R_5 and R_7 is independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_{16}-C_{30} linear alkyl-, RO-, -NRR', -PRR', -SR, fluoro substituted forms thereof, and perfluoro forms thereof; where R and R' are each independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; and M is B, Al, Ga or In; or a composition of the formula:



V

where M^1 is Ti, Zr or Hf; each of R_8, R_9 and R_{10} is independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, amide, alkoxide, phenoxide, phosphinimide, cyclopentadienyl, indenyl, fluorenyl derivatives, RO-, -NRR', -PRR', -SR, fluoro substituted forms thereof, and perfluoro forms thereof; where R and R' are each independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; and R_{11} is C_1-C_{20} alkyl linear or branched with the proviso that R_{11} is a better leaving group than any of R_8, R_9 or R_{10} under nucleophic attack by a hydrogen or other alkyl abstracting agents to yield a cationic M^1 species.

7. The composition of claim 6 wherein A is P and M is B.

8. The composition of claim 6 or 7 wherein R_3 and R_4 are identical perfluorinated groups and R_5 is perfluorinated.

9. The composition of claim 7 wherein R_1-R_5 are all one of C_6-C_{18} aryl, C_6-C_{18} having perfluorinated C_6-C_{18} aryl.

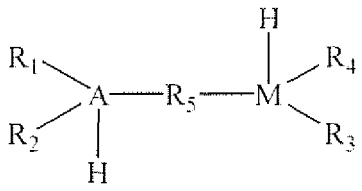
10. The composition of claim 7 wherein R_1 and R_2 are both 2,4,6-$(CH_3)_3$ C_6H_2.

11. The composition of claim 6 wherein said composition of formula II and said composition of formula III or V are dissolved in a solvent.

12. The composition of claim 6 wherein said composition of formula II or V and said composition of formula III form a coating on a support.

13. A process for reversibly dissociating and binding hydrogen comprising exposing hydrogen to a compound of claim 1 or a composition of claim 2 under conditions that induce binding.

14. A compound of the formula:



IV

where each of R_1, R_2, R_3 and R_4 is independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_{16}-C_{30} linear alkyl-, RO-, -NRR', -PRR', -SR, fluoro substituted forms thereof, and perfluoro forms thereof; and R_5 is C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_3-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; where R and R' are each independently C_6-C_{18} aryl-, C_5-C_8 cycloalkyl-, C_6-C_{18} aryl having at least one C_1-C_{20} alkyl substituent, C_5-C_8 cycloalkyl having at least one C_1-C_{20} alkyl substituent, C_4-C_{20} branched alkyl-, C_2-C_{30} linear alkyl-, fluoro substituted forms thereof, and perfluoro forms thereof; A is N, P, S, or O with the proviso that when A is S, R_2 is a nullity; and M is B, Al, Ga or In.

15. The compound of claim 14 wherein A is P and M is B.

16. The compound of claim 14 or 15 wherein R_3 and R_4 are identical perfluorinated groups and R_5 is perfluorinated.

17. The compound of claim 15 wherein R_1-R_5 are all one of C_6-C_{18} aryl, C_6-C_{18} having perfluorinated C_6-C_{18} aryl.

18. The compound of claim 15 wherein R_1 and R_2 are both 2,4,6-$(CH_3)_3$ C_6H_2.

19. A process of catalytic hydrogenation of a substrate comprising: independently compound I, a mixture of II and III, compound III, a mixture of II and V or a mixture of II and IV together with dihydrogen and solvent form a catalyst whereby hydrogenation of a substrate is effected.

20. A process wherein independently compound I, a mixture of II and III, compound III, a mixture of II-V or a mixture of II and IV and a sacrificial dihydrogen source solvent form a catalyst that affect hydrogenation transfer resulting in the hydrogenation of a substrate.

21. The process of claim 19 or 20 wherein the substrate and a reduction product therefrom is

Substrates	**Reduction Product**
Ketimine to	Amine,
Ketene-imine to	Amine
Aldimine to	Amine,
Nitrile to	Amine,
Aziridine to	Amine,
Olefin to	Hydrocarbon,
Ketone to	Alcohol,
Aldehyde to	Alcohol,
Borazines to	borane-amine adduct,
Acetylene to	Hydrocarbon,
Enols to	Alcohol,
Enamines to	Amine,

Ketene to	Alcohol,
Allene to	Alkane,
Ester to	Alcohol,
Epoxide to	Alcohol,
Isocyanide to	Amine, or
Lactone to	Diol.