

SELECTIVE, CATALYTIC, AND THERMALLY INDUCED FUNCTIONALIZATION OF PRIMARY C-H BONDS
IN HYDROCARBONSField of the Invention

The present invention relates to the selective functionalization of a hydrocarbon at its primary C-H site by thermally reacting a functionalizing reagent and the hydrocarbon in the presence of an transition metal catalyst.

Background of the Invention

Aliphatic compounds, and especially alkanes, are among the most abundant but least reactive molecules. Chemical synthesis relies on reactions that form one product selectively, and few reactions involving aliphatic compounds, such as alkanes, occur in this fashion. Radical reactions, such as halogenations and autoxidations, typically produce mixtures of products; even enzymes do not react regiospecifically with linear alkanes. Transition metal compounds are known to react with alkanes to give terminal alkyl complexes selectively, but these reactions are typically stoichiometric in metal. Transition metal-catalyzed dehydrogenation suffers from unfavorable thermodynamics and isomerization of terminal to internal alkenes during the reaction. Carbonylation of alkanes is also endothermic, and the photochemical processes produce secondary photoproducts.

Several years ago, it was reported in K.M. Waltz, C.N. Muhoro, J.F. Hartwig, Organometallics, 1999, 21 and

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in K. Waltz, J.F. Hartwig, Science 1997, 277, 211, that low valent transition metal complexes containing boryl ligands reacted with hydrocarbons, including alkanes, by photochemical dissociation of ligand to produce functionalized hydrocarbons. It was reported that organoboronate esters were formed in a stoichiometric fashion by the regiospecific replacement of one hydrogen on a terminal position with a boryl group.

It was also reported in H.Chen, J.F. Hartwig, Angew.Chem.Int.Ed.Engl 1999 that commercially available R_2BBR_2 (R_2 =pinacolate) reagents and substituted cyclopentadienyl (Cp^*) $Re(CO)_3$ would catalytically convert alkanes to alkylboronate esters under photochemical reaction conditions. Photochemical processes, however, are impractical at an industrial scale.

It is desirable to functionalize regiospecifically an aliphatic compound at its terminal C-H site. It is also desirable that the process for the functionalization occur thermally rather than through other means such as photochemical processes.

It is highly desirable to manufacture a functionalized aliphatic compound, and especially a functionalized alkane, by a process which is catalytic rather than stoichiometric in metal.

Summary of the Invention

The present invention provides a process for selectively functionalizing an aliphatic hydrocarbon and/or alkyl branched alicyclic hydrocarbon at a primary C-H hydrocarbon bond comprising thermally reacting a

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functionalizing reagent and the hydrocarbon in the presence of a catalyst, said catalyst comprising:

- a) a source of a transition metal;
- b) a source of a 3 to 8, cyclic or non-cyclic, aromatic or non-aromatic, neutral, cationic or anionic, substituted or unsubstituted, electron donor moiety which does not dissociate under thermal reaction conditions, wherein said moiety
 - (i) lacks aromatic C-H bonds on the moiety directly bonded to the transition metal, or
 - (ii) contains sterically hindered aromatic C-H bonds on the moiety directly bonded to the transition metal; and
- c) a source of ligands capable of formally donating an electron pair to the transition metal of a) and which dissociate thermally;

and wherein said functionalizing reagent comprises a source of boron.

Detailed Description of the Invention

The process of the present invention is 80% or more selective toward functionalizing a primary C-H bond on hydrocarbon molecules, is catalytic, and relies on thermal rather than photolytic or photochemical processes to supply the activation energy required for dissociating the ligand from the catalyst.

The reaction proceeds in a straightforward manner in that a hydrocarbon, a catalyst, and a functionalizing reagent are contacted in a reaction vessel and heated to a temperature effective to activate the reaction towards

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the functionalization of the hydrocarbon at its primary C-H site.

The nature of the catalyst and functionalizing reagent as described in further detail below enable one to manufacture selectively and thermally a hydrocarbon functionalized at its primary C-H site.

The catalyst used in the reaction must be one which is capable of being thermally activated, and the process functionalizes the primary C-H bond of a hydrocarbon by thermally activating the catalyst.

By "thermal activation" of the catalyst is meant the process of dissociating a c) ligand from a metal centre by application of heat below the temperature at which the Z ligand (described below) dissociates from the metal centre, and at least above the temperature of the environment at which the functionalizing reagent is stored.

A useful screening technique to determine whether a catalyst will activate a primary C-H bond is as follows. The catalyst one desires to employ is mixed with a deuterated ligand at a molar ratio within the range of from 1:1 to 1:10 in the presence of an appropriate solvent, such as decane or cyclohexane-d₁₂. The mixture is analyzed by ³¹P NMR, ¹¹B NMR, ¹H NMR, and ²H NMR. The mixture is subsequently reacted solely by application of heat for 48 hours or less at no more than reaction pressures and at a temperature at which reaction takes place but below the temperature at which the b) moiety and c) ligands dissociate from the metal centre. Analytical results of a catalyst which has been thermally

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activated will show the formation of a peak corresponding to free dissociated ligand and the formation of a deuterated catalyst, and the reduction or elimination of peaks corresponding to the presence of free deuterated
5 ligand.

A useful screening test to determine whether a catalyst is one which is capable of being activated thermally is to conduct the reaction in the dark.

Although other compounds which chemically react to
10 assist the dissociation of the c) ligand may be used along with the catalyst in the process of functionalizing an hydrocarbon, the catalyst used in the process must be of a type which is capable of being thermally activated in the absence of any compound which chemically reacts
15 with the reagent to assist the activation of the reagent.

Accordingly, a process which applies heat in addition to other activation mechanisms, such as chemical or photolytic means, and successfully activates the catalyst is nevertheless a process within the scope of
20 the invention if the particular catalyst is capable of thermally functionalizing the hydrocarbon at a primary C-H bond in the absence of a co-catalyst or photons.

Other published catalytic systems for activating alkanes at the primary C-H bond require the presence of a
25 sacrificial olefin to achieve high turnover numbers. An advantage of the process of the present invention is that a sacrificial hydrogen acceptor is not required to provide a catalytic process with high turnover. Hydrogen released from the primary C-H hydrocarbon bond does not
30 readily react with the functionalized hydrocarbon under

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reaction conditions. Although the presence of hydrogen acceptors is not excluded from the invention, the process of the invention is capable of achieving high turnover numbers in the absence of a sacrificial hydrogen acceptor.

By a "functionalizing reagent" is generically meant to include any compound as described below which operates to functionalize a hydrocarbon's primary C-H bond, and is not meant to define the reaction mechanism, efficiency, or fate of the reagent compound itself.

Suitable hydrocarbon substrates which are functionalized in the process of the invention are any hydrocarbons containing a primary C-H bond, also known as its terminal C-H bond.

By "functionalized" is meant the replacement of H at a primary C-H bond of a hydrocarbon with the functionalizing reagent residue.

By a "primary C-H bond" is meant any bond between a hydrogen atom and any carbon atom bearing two or more additional hydrogen atoms. The primary C-H bond is to be distinguished from a secondary C-H bonding site, wherein the carbon atom is a secondary carbon atom and any functional group replacing its hydrogen atom would be considered a secondary functional molecule.

It is to be understood that a "bond" as used throughout the specification means a covalent bond, a complex, a coordination, or any other form of a linkage between the stated atoms.

A hydrocarbon which is functionalized in the process of the invention is a saturated or unsaturated, branched

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or unbranched, substituted or unsubstituted aliphatic hydrocarbon (e.g. alkanes or alkenes); or a saturated or unsaturated, substituted or unsubstituted, alkyl branched alicyclic compounds, each having at least one primary C-H bond, and which do not deactivate the catalyst at reaction temperatures.

The hydrocarbons may be used singly or in mixture.

The hydrocarbon composition contains aliphatic and/or alkyl branched alicyclic hydrocarbons, optionally mixed with other hydrocarbon molecules, such as aromatic compounds.

The hydrocarbon composition preferably comprises at least 50 wt.% aliphatic and/or alkyl branched alicyclic hydrocarbons, preferably at least 75 wt.%, more preferably at least 90 wt.%, and most preferably at least 95 wt.% or more up to 100 wt.%.

The source of the hydrocarbon can be any commercial source available, such as from a refined crude oil source or a Fisher-Tropsch stream, and can be used in crude mixtures or at any level of refinement, any fraction containing alkanes, and at any purity.

Further, any olefin having from 3 to 30 carbon atoms, and their dimers or trimers, are also useful hydrocarbons provided that the molecule has a terminal site having one saturated carbon atom.

Alkyl branched alicyclic (e.g. branched cycloparaffins or cycloolefins) are also useful, so long as the alkyl group contains at least one saturated carbon atom containing a primary C-H bond site.

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In one embodiment, the hydrocarbon comprises a linear or branched alkane (by definition, having no unsaturation, cyclic or aryl moieties attached). Suitable examples of alkanes may include those having
5 from 1 to 32 carbon atoms, preferably from 3 to 24 carbon atoms, and more preferably from 6 to 18 carbon atoms.

Examples of linear hydrocarbons include n-hexane, n-heptane, n-octane, n-nonane, n-dodecane, n-tridecane, n-
10 tetradecane, n-pentadecane, n-hexadecane, n-heptadecane, n-octadecane, n-nonadecane, n-eicosane, and the like.

Examples of branched aliphatic hydrocarbons include 2,2,3,3-tetra-methylbutane, 2,2,4-trimethylpentane, n-tricontane, 2-methylbutane, 2-methylpentane, 3-
15 methylpentane, 2-methylhexane, 3-methylhexane, 2-methylheptane, 3-methylheptane, 4-methylheptane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane, 2,2-dimethylhexane, 2,4-dimethylhexane,
20 2,5-dimethylhexane, 3,4-dimethylhexane, 2,3-dimethylheptane, other 2-methyl or ethyl-C₆-C₂₈ alkanes, mixtures thereof, and the like.

Examples of alkyl branched alicyclic hydrocarbons include methyl cyclohexane, methyl cyclooctane, ethyl
25 cyclohexane, ethyl cyclooctane, isopropyl cyclohexane, and the like.

The hydrocarbon may contain heteroatoms within the hydrocarbon chain, such as oxygen or nitrogen. However, generally the number of heteroatoms will be no more than
30 1 heteroatom for every 4 carbon atoms, preferably no more

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than 1 heteroatom for every 6 carbon atoms, and more preferably the hydrocarbon will be free of heteroatoms.

The catalyst used in the process of the present invention comprises:

- 5 a) a source of a transition metal;
- b) a source of a 3 to 8, cyclic or non-cyclic, aromatic or non-aromatic, neutral, cationic or anionic, substituted or unsubstituted, electron donor moiety which does not dissociate under thermal reaction conditions, wherein said moiety
 - 10 (i) lacks aromatic C-H bonds on the moiety directly bonded to the transition metal, or
 - (ii) contains sterically hindered aromatic C-H bonds on the moiety directly bonded to the
 - 15 transition metal; and
- c) a source of ligands capable of formally donating an electron pair to the transition metal of a) and which dissociate thermally.

Preferably, the source of c) ligands comprise

20 trialkylsilanes, unsaturated aliphatic compounds, π allyl compounds, or π arene compounds, wherein said π arene compounds

- (i) lack aromatic C-H bonds on the moiety directly bonded to the transition metal, or
- 25 (ii) contains sterically hindered aromatic C-H bonds on the moiety directly bonded to the transition metal.

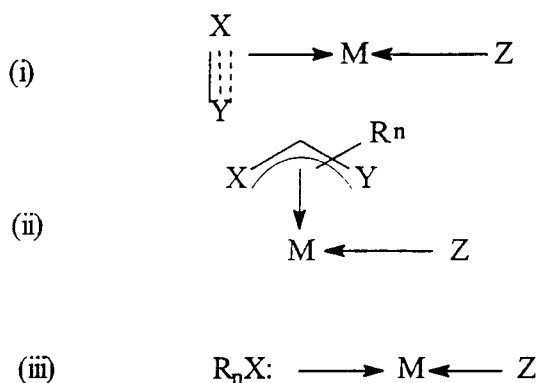
A more preferred catalyst for use in the process of the present invention comprises, or is obtained by

30 combining a source of the following in any sequence:

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- a) Rh or Ir;
 b) a fully substituted cyclic C_s moiety having a π-coordinated electronic structure and lacking aromatic C-H bonds; and
 5 c) ligands comprising aliphatic unsaturated or π arene compounds, and wherein said π arene compounds
 (i) lack aromatic C-H bonds on the moiety directly bonded to the transition metal, or
 (ii) contain sterically hindered aromatic C-H
 10 bonds on the moiety directly bonded to the transition metal.

In an embodiment of the present invention, the catalyst can be conveniently represented by any one of the following structures:



wherein X and Y together represent the c) ligands bonded directly or indirectly to M, and wherein X and Y may be bridged to form a cyclic arene compound which may contain
 20 branches, substituents, or fused aromatic rings; M represents the transition metal centre of a); Z represents a cyclic or non-cyclic, aromatic or non-

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aromatic, neutral, cationic or anionic, substituted or unsubstituted electron donor moiety b) having a π -coordinated electronic structure and lacking aromatic C-H bonds on the moiety which will directly bond to the transition metal of a) or containing sterically hindered aromatic C-H bonds, R represents one or more optional substituents or branches, and n represents an integer ranging from 0 to 8.

One or more of the ligands are bonded to the transition metal centre M, and preferably more than one ligand is bonded to the transition metal centre M. It is not critical to the invention that either the nature or location of the linkage between the ligands to the transition metal centre M be known, so long as some form of a linkage between the X or the X and Y ligands and the transition metal centre M exists at a position which will provide a catalyst which is effective to functionalize a primary C-H hydrocarbon bond.

Suitable transition metals of a) (or M) include transition metals in the +1, +2, +3, +4, +5, or +6 oxidation state. It is preferred to employ a transition metal that is capable of traversing 2 or more formal oxidation states, more preferably 4 or more formal oxidation states. Accordingly, it is preferred to employ a metal having a formal oxidation state prior to bonding with the b) compound and the c) ligand(s) of +4, +5, or +6.

Examples of suitable transition metals include Fe, Co, Ni, Rh, Ru, Os, Pt, Pd, Mn, Re, W, Cr, Mo, Ir, and the metals from the lanthanide and actinide series.

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Preferred metals are Re, Rh, and Ir. More preferred are Rh and Ir, and most preferred is Rh to improve the reaction rate over Ir and to improve the conversion of the functionalizing reagent to the hydrocarbon-
5 functionalizing reagent adduct and other byproducts.

It is generally believed that Ir transition metal centres promote faster reaction rates and are more completely convert C-H bonds than Rh using equivalent ligands and reaction conditions. Surprisingly, however,
10 it has now been found that the reaction rate using Rh as a transition metal centre to convert the functionalizing reagent to the functionalized hydrocarbon was faster and more complete than its Ir counterpart. Accordingly, in a most preferred embodiment, the transition metal is Rh.

15 The Z moiety depicted in the structural diagrams above (corresponding to the b) moiety) is a 3-8 electron donor ligand which does not dissociate under thermal reaction conditions.

"Thermal reaction conditions" are all the physical
20 reaction conditions employed in practice to functionalize the hydrocarbon at its primary C-H site, including, but not limited to the pressure, temperature, space velocity, etc., conditions within the reaction vessel.

Dissociation of the Z moiety results in the
25 degradation of the catalyst, thereby terminating its activity.

The Z moiety also donates electron density to stabilize the oxidation state of the transition metal of the active catalyst. Preferably, the electronic charge
30 of the Z moiety will fully stabilize the metal centre

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depending upon the oxidation state of the metal centre M in its active state.

The Z moiety may be between an η^2 and an η^8 complexed cyclic or non-cyclic, aromatic or non-aromatic, neutral cationic or anionic, substituted or unsubstituted ligand. It is preferably a π coordinated, cyclic fully substituted aromatic compound, and more preferably a cyclic, fully substituted aromatic, anionic moiety.

In one embodiment, the Z moiety is a fully substituted cyclic η^5 - η^6 5-8 carbon membered ring.

The Z moiety may be coordinated to the transition metal centre M in several different isomeric configurations. For example, the Z moiety in the η^5 configuration may be in one of the S, W, or U isomeric states. In a more preferred embodiment, the Z moiety is the U isomer in the η^5 bonded configuration. It is to be understood that the original position of the double bonds of a dienylyl ligand need not be identified because of the delocalization effect. For example, an η^5 -1,3-pentadien-3-yl group is identical to the η^5 -1,4-pentadien-3-yl group. It is to be further understood that all isomeric forms of Z moieties are included in any reference to a Z moiety identified herein. Furthermore, it is not critical to the invention that either the nature of the linkage between the Z moiety and the transition metal centre M, or the carbon number to which the Z moiety is coordinated, bonded, or complexed to the transition metal centre M, be known, so long as some form of a linkage between the Z moiety and the transition metal centre M exists at a position which will provide a functionalizing

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reagent which is effective to functionalize a terminal C-H bond.

As mentioned previously, the Z moiety (equivalent to moiety b)) must lack aromatic C-H bonds on the moiety directly bonded to the transition metal, or contain
5 sterically hindered aromatic C-H bonds on the moiety directly bonded to the transition metal.

An "aromatic C-H bond" is a bond between a hydrogen atom and one of the carbon atoms forming the aromatic
10 ring. The presence of sterically accessible aromatic C-H bonds on the Z moiety which will directly bond to the transition metal a) is undesirable because they compete with the functionalization of the primary C-H hydrocarbon bonds, thereby reducing the yield of functionalized
15 hydrocarbon.

Accordingly, the Z moiety should either lack aromatic C-H bonds altogether on the moiety directly bonded to the transition metal, or if such aromatic C-H bonds are present, they should be sterically inaccessible by other
20 activated catalyst molecules in the vicinity in order to minimize or avoid functionalizing the Z moiety aromatic C-H sites.

In a more preferred embodiment, every site on the Z moiety, including those sites which are directly and only
25 indirectly bonded to the transition metal through a substituent on the Z moiety directly bonded to the transition metal, are either lacking in any aromatic C-H bonds or contain sterically hindered C-H sites.

It will be appreciated that suitable substituents are
30 bulky groups which are generally regarded as sterically

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demanding. Non-limiting examples of such bulky substituents on aromatic ring carbon atoms adjacent to the aromatic C-H site include hydrocarbyl, hydrocarbyl substituted metalloids wherein the metalloid is selected from Group IV A of the Periodic Table, silyl, 5 germyl, cyano, hydroxyl, amino, and halo groups, such as fluorine or chlorine, especially fluoro or fluoroalkyl groups, aryl, phenyl which optionally may bear one or more of the same or different substituents, alkylaryl, 10 alkoxy, phenoxy, phenylalkoxy, benzyl, bulky substituents containing one or more hetero atoms such as tri (loweralkyl)silyl, -NPh₂, -NHPh, -BPh₂, and -B(OPh)₂, wherein n may be an integer of from 0 to 4, preferably from 0 to 2 and more preferably from 0 to 1, and m may be 15 an integer of from 0 to 3, preferably from 0 to 2 and more preferably from 0 to 1, and carboxylic acid esters.

Any of the Z moiety substituents may be joined together on the Z moiety to form a C₄-C₂₀ saturated ring. Examples of hydrocarbyl groups include C₁-C₂₀ branched or 20 unbranched alkyl groups, preferably C₁-C₆ branched or unbranched alkyl groups such as methyl, ethyl, isopropyl, propyl, butyl, t-butyl, isobutyl, neopentyl, and 3-phenyl-neopentyl. Other examples of hydrocarbyl groups include the C₁-C₂₀ substituted radicals, optionally 25 where one or more of the hydrogen atoms may be replaced with a halogen radical, an amido radical, a phosphino radical, and an alkoxy radical or any other radical containing a Lewis acidic or basic functionality.

It is preferred that the substituent donate electron 30 density to the ligand. Such substituents generally

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contribute to increasing the thermal stability of the catalyst under reaction conditions with the hydrocarbon, as well as increasing the activity of the catalyst.

Examples of preferred substituents comprise
5 trimethylsilyl and C₁-C₄ branched or unbranched alkyl groups, such as methyl, isopropyl, t-butyl.

The number of substituents is sufficient to create a fully substituted Z moiety or sufficiently substituted to sterically protect the remaining aromatic C-H bonds. The
10 aromatic carbon atoms which are substituted include those carbon atoms in aromatic nuclei fused to an aromatic ring bonded directly to the metal centre M, as well as the aromatic nuclei indirectly tethered to the transition metal through the non-dissociating electron donating
15 atoms directly bonded to the transition metal.

In one embodiment, the b) moiety contains no aromatic C-H bonds. Preferably, the b) moiety is fully substituted with C₁-C₄ alkyl groups.

In another embodiment the b) moiety comprises a fully
20 substituted η^5 cyclopentadienyl moiety, preferably a η^5 pentamethyl cyclopentadienyl moiety.

Examples of b) moieties (equivalent to the Z moieties) include, but are not limited to, methylcyclopentadiene, ethylcyclopentadiene, t-
25 butylcyclopentadiene, hexylcyclopentadiene, octylcyclopentadiene, 1,2-dimethylcyclopentadiene, 1,3-dimethylcyclopentadiene, 2,4-dimethyl- η^5 -pentadien-1-yl, 1, 5-dimethyl- η^5 -pentadien-2-yl, 2, 4-dimethyl- η^5 -pentadien-3-yl, 1, 5-dimethyl- η^5 -pentadien-3-yl, 1,2,4-
30 trimethylcyclopentadiene, pentamethylcyclopentadiene, 1,

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5-bis(trimethylsilyl)- η^5 -pentadien-3-yl, 1,2,3,4-tetramethylcyclopentadiene, 1, 2, 6, 6-tetramethyl- η^5 -cyclohexadien-4-yl, 1,2,4,6,6-pentamethyl- η^5 -cyclohexadien-3-yl, 1, 2, 4, 6, 6-pentamethyl- η^5 -cyclohexadien-5-yl, 1, 2, 5, 6, 6-pentamethyl- η^5 -cyclohexadien-4-yl, 1, 2, 4, 5, 6, 6-hexamethyl- η^5 -cyclohexadien-3-yl; 1,2, 4, 5-tetramethyl-6, 6-cyclotrimethylene- η^5 -cyclohexadien-3-yl; 1, 2-dihydronaphthalen-1-yl; 1, 2-dihydronaphthalen-2-yl;
10 1,1-dimethyl-1,2-dihydronaphthalen-2-yl; 1, 1-dimethyl-1,2-dihydronaphthalen-4-yl; diphenylmethyl- di(1-cyclohexenyl)methyl; 1, 1-dimethyl-1,2, 5, 6, 7, 8-hexahydronaphthalen-4-yl; 1, 1-dimethyl-1,4, 5, 6, 7, 8-hexahydronaphthalen-4-yl; 1, 1-dimethyl-1,5, 6, 7, 8, 9-hexahydronaphthalen-4-yl; 1,1,2,3-tetramethyl-1,2, 5, 6, 7, 8-hexahydronaphthalen-4-yl; 1,1,2,3-tetramethyl-1,4, 5, 6, 7, 8-hexahydronaphthalen-4-yl; 1, 1,2, 3-tetramethyl-1, 5, 6, 7, 8, 9-hexahydronaphthalen-4-yl; 9, 10-dihydroanthracen-9-yl; 9,10-dihydroanthracen-1-yl; 9, 9-dimethyl-9, 10-dihydroanthracen-10-yl; 1,2,3,4,9, 10-hexahydroanthracen-9-yl; 1,2, 3, 4, 9,10-hexahydroanthracen-1-yl; 1,2, 3, 4, 9, 11-hexahydroanthracen-9-yl; 1,4, 5, 8, 9, 10-hexahydroanthracen-1-yl; 9, 9-dimethyl-1,4, 5, 8, 9, 10-hexahydroanthracen-10-yl; 9, 9-dimethyl-1,4, 5, 8, 9, 10-hexahydroanthracen-2-yl; 8, 8-dimethyl-1,4, 5, 8, 9,10-hexahydroanthracen-10-yl; 1,2, 3, 4, 5, 6, 7, 8, 9,10-decahydroanthracen-9-yl; 1,2, 3, 4, 5, 6, 7, 8, 9,11-decahydroanthracen-9-yl; 9, 9-dimethyl-1,2, 3, 4, 5, 6, 7, 8, 9,10-decahydroanthracen-10-yl; 9, 9-dimethyl-1,2,

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3, 4, 5, 6, 7, 8, 9,11-decahydroanthracen-10-yl, 4,7-
dimethylindene, 4,5,6,7-tetrahydroindene; 3-
methylcyclopentadienylsilane, 1,2-
dimethylcyclopentadienylsilane, 1,3-
5 dimethylcyclopentadienylsilane, 1,2,4-
trimethylcyclopentadienylsilane, 1,2,3,4-
tetramethylcyclopentadienylsilane,
pentamethylcyclopentadienylsilane, 1,2,4-
trimethylindenylsilane, 1,2,3,4-tetramethylindenylsilane
10 and pentamethylindenylsilane and each of their equivalent
ligands.

Other Z moieties include the fully substituted or
sterically hindered substituted moieties of the compounds
identified in U.S. Patent No. 5,541,349 as the L ligand
15 therein, which disclosure is fully incorporated herein by
reference.

When Z is cyclic, the ring may optionally be
comprised of heteroatoms, such as nitrogen or oxygen. Z
can be a 4-50 member non-hydrogen atom group, preferably
20 a 4-10 membered fully substituted cyclic moiety or a
sterically hindered moiety comprised of a single or fused
ring system. Examples of any of the above compounds
bonded through an alkylene group (usually 2 to 8,
preferably 2 to 3, carbon atoms) are suitable as the Z
25 moiety.

Examples of such compounds include bis(4,5,6,7-
tetrahydro-1-indenyl)ethane, 1,3-propanedinylbisindene,
1,3-propanedinylbis(4,5,6,7-tetrahydro)indene,
propylenebis(1-indene), isopropyl(1-
30 indenyl)cyclopentadiene, diphenylmethylen(9-

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fluorenyl)cyclopentadiene, isopropylcyclopentadienyl-1-fluoreneisopropylbiscyclopentadiene.

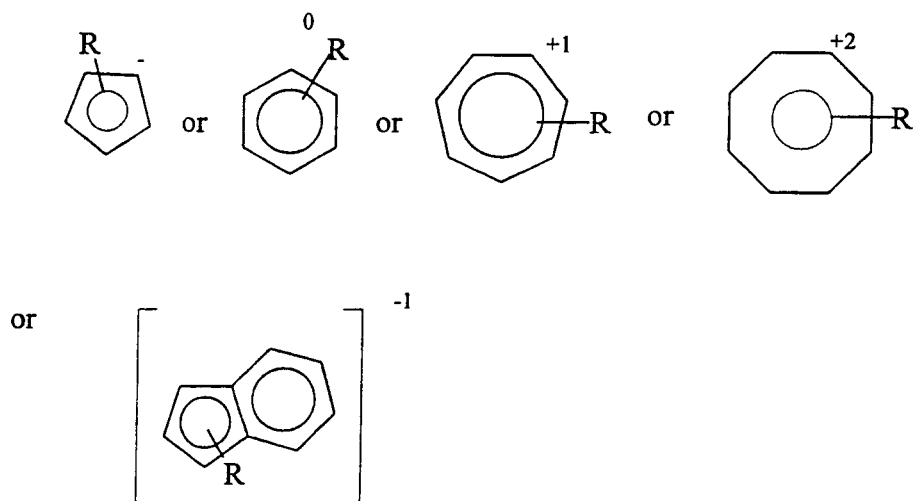
A mixture of any of the aforementioned compounds may be used in the synthesis of the catalyst.

5 Most preferred as the Z moieties are alkyl substituted cyclopentadienyl compounds, and in particular the C₁-C₄ alkyl substituted cyclopentadienyl compounds such as the mono, di, tri, tetra, or penta methyl, ethyl, propyl, isopropyl, or t-butyl cyclopentadienyl
10 compounds (e.g. dimethylcyclopentadienyl, methylcyclopentadienyl, tetramethylcyclopentadienyl, diethylcyclopentadienyl, t-butylcyclopentadienyl, and pentamethylcyclopentadienyl) and the hydroxy and C₁-C₄ alkyl substituted indenyl and fluorenyl compounds, such
15 as tetramethylindenyl, tetrahydrofluorenyl, and octahydrofluorenyl.

Some examples of cyclic Z moiety structures are represented below:

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wherein Z is fully substituted with R groups or sufficient numbers of R groups to sterically hinder the aromatic C-H bonds. The number of R groups may range from 1 to 8.

The catalyst used in the process of the invention is also comprised of one or more c) ligands. The catalyst contains at least one c) ligand, and preferably contains 2 or more c) ligands. The c) ligand is derived from a source of ligands capable of formally donating an electron pair to the transition metal a) and which dissociate thermally.

The c) ligand is derived from sources which donate electron density to the transition metal and which contain either a non-bonding pair of electrons or a bonding pair of electrons. By "donating" a pair of electrons is meant that the ligand does not transfer electrons to the metal, and upon dissociation, the electrons leave with the ligand. It is not necessary that the bond linkage occur between a coordinating atom and the transition metal centre M. The bond linkage may

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occur between the transition metal centre M and a π bond or a π coordinated ring, each of which can donate electron density to stabilize the oxidation state of the transition metal centre M, or the bond linkage may be a σ bond between a ligand atom and the transition metal centre M.

The c) ligand should be one which dissociates from the catalyst upon application of thermal energy. Since it is desirable to both increase product yield and reaction rates, not all of the ligands should be of the type which are tightly held to the transition metal centre, and not all ligands should dissociate from the catalyst slowly or only at temperatures approaching the decomposition temperature of the catalyst. Accordingly, at least one of the ligands should thermally dissociate from the catalyst.

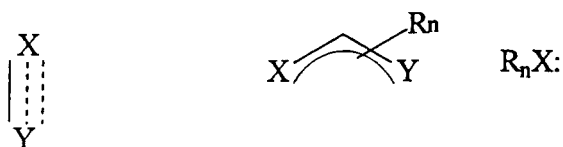
By "thermally dissociating" is meant that the ligand is capable of dissociating from the transition metal centre M using thermal energy at temperatures below the temperature at which the b) moiety dissociates from the transition metal centre M, which would result in the degradation of the catalyst.

In a preferred embodiment, the c) ligand dissociates from the metal centre a) at temperatures in the range of from 70°C to 250°C. Evidence of thermal dissociation is to conduct the reaction in a dark room and in the absence of any co-catalyst or other ingredients beside the functionalizing reagent, the catalyst, the hydrocarbon, and a solvent.

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In one embodiment, the c) ligand comprises aliphatic unsaturated or π arene compounds, said π arene compounds lacking π arene C-H bonds.

The c) ligand can be broadly represented by the
 5 following structural formulae:

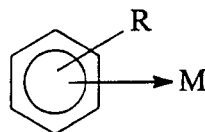


wherein X and Y each independently represent one or more of H, C, B, S, N, Si, Sn, P, and As and combinations thereof, to which saturated or unsaturated, branched or
 10 unbranched alkyl, aromatic, alicyclic, or alkaryl groups may be bonded, and wherein X and Y may be bridged to form a cyclic arene compound which may contain branches, substituents, or fused aromatic rings, R represents hydrogen or one or more optional branches or
 15 substituents, and n represents an integer ranging from 0 to 8.

The unsaturation between X and Y may be olefinic, aromatic or acetylenic. However, X and Y may also be bound by a single covalent bond when X or Y is hydrogen.

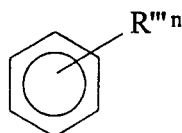
20 An example of a fused X-Y structure is represented by a 6 membered aromatic ring as shown in the structure below:

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The c) ligand may be conveniently represented by the following structural formula:

5



wherein R''' independently represents hydrogen or a saturated or unsaturated, branched or unbranched alkyl or alkaryl group having from 1 to 15 carbon atoms or one or more fused ring structures, and n represents the number of R''' groups and is an integer ranging from 2 to 6.

10

In a preferred embodiment, R''' is a saturated, branched or unbranched C₁-C₄ alkyl and n is an integer ranging from 3 to 6.

15

It is particularly preferred that c) ligand comprises an η^4 hexamethylbenzyl group.

20

Preferred c) ligands satisfying the above criteria may be derived from a source of :PR₃, :NR'₃, HSiR₃, unsaturated aliphatic compounds, π allyl, and π arene compounds. More preferred c) ligands comprise a source of HSiR₃, unsaturated aliphatic compounds, π allyl and π arene compounds. Most preferred are the unsaturated aliphatic compounds, π allyl compounds, and the π arene

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compounds, and especially the unsaturated aliphatic compounds and the π arene compounds.

Tertiary phosphines suitable as the c) ligand include the mono and bisphosphines. Monophosphines are
5 represented by the formula:



wherein R is independently an aromatic of up to 14 carbon atoms, optionally substituted; or a C₁-C₄₀ alkyl or alicyclic group, optionally containing atoms other than
10 carbon and hydrogen in the form of monovalent substituents which are preferably electron-withdrawing substituents such as halo, preferably the middle halogens chloro and bromo, nitro and trifluoromethyl. Examples of aromatic R groups include phenyl, tolyl and naphthyl.

15 The aromatic groups are optionally substituted aryl groups with halogen atoms and alkyl, aryl, alkoxy, carboxy, carbalkoxy, acyl, trihalogenmethyl, cyano, dialkylamino, sulphonylalkyl and alkanoyloxy groups.

Other specific examples of suitable phosphines are
20 bis(1,1-dimethylethyl) phenylphosphine, dimethylphenylphosphine, cyclohexyldiphenylphosphine, dibutylphenylphosphine, methyldiphenylphosphine, triphenylphosphine, tri-n-butylphosphine, tris(4-tolylphosphine), tris(4-chlorophenyl)phosphine, tris(4-methoxyphenyl)phosphine, tris(3-methoxyphenyl)phosphine,
25 tris(2-methoxyphenyl)phosphine, tris(4-butylphenyl)phosphine, tris(4-trifluorophenyl)phosphine, tris(4-fluorophenyl)phosphine and 2-carboxyphenyl diphenylphosphine, tri-p-tolylphosphine, tri-p-methoxyphenylphosphine, o-diphenylphosphinobenzoic acid,
30

- 25 -

and in particular triphenylphosphine, tributylphosphine, trimethylphosphine, triethylphosphine, tripropylphosphine, and any C₁-C₆ alkyl combination as an R' group, 1,2-bis (diphenyl-phosphino) ethane, 1,2-bis(diphenylphosphino) ethene, 1,3-bis (diphenylphosphino) propane, 1,3-bis(diethylphosphino) propane, 1,4-bis (diphenylphosphino) butane, 1,3-bis(di-isopropylphosphino) propane and 1,3-bis (di-p-methoxyphenyl phosphino) propane.

Tertiary amines suitable as the c) ligand are represented by the formula:



wherein R' has the same meaning as R above with respect to :PR₃, as well as the polyamines such as the diamines, triamine, and pentamines.

Examples of electron donating c) amine ligands include trimethylamine, triethylamine, tri-n-propylamine, triisopropylamine, tri(n-butyl)amine, tri(isobutyl)amine, N,N-dimethylaniline, tributylamine, benzyldimethylamine, tris(dimethylaminomethyl)phenol, dimethylethanolamine, n-methylmorpholine, triethylene diamine, N-methylmorpholine, N-ethylmorpholine, diethyl-ethanolamine, N-cocmorpholine, 1-methyl-4-dimethyl-amino-ethylpiperazine, 3-methoxypropyldimethylamine, N,N,N'-tri-methylisopropyl propylenediamine, 3-diethylamino propyl-diethylamine, dimethylbenzylamine, dimethylcyclohexylamine, 2-methylimidazole, 2-phenylimidazole, 2-ethyl-4-methyl imidazole, 2,4,6-tris(dimethylaminomethyl)phenol, 1,4-

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diazabicyclo(2,2,2)-octane, 1,5-diazabicyclo(5,4,0)-undecane, dimethyldodecylamine, pyridine, 4-(1-butylpentyl)pyridine, quinoline, isoquinoline, lipdine, quinaldine, nonylpyridine, 2,6-lutidine, 2,4,6-collidine, 2-undecylimidazole, 2-heptadecylimidazole, 2-phenylimidazole, 2-ethyl-4-methylimidazole, 1-benzyl-2-methylimidazole, 1-propyl-2-methylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-ethyl-4-methylimidazole, 1-cyanoethyl-2-undecylimidazole, 1-cyanoethyl-2-phenylimidazole, 1-guanaminoethyl-2-methylimidazole, N,N-dimethylaniline, N,N-dimethyltoluidine, N,N-dimethyl-p-anisidine, p-halogeno-N,N-dimethyl-aniline, 2-N-ethylanilino ethanol, tri-n-butylamine, pyridine, quinoline, N-methylmorpholine, triethanolamine, and N,N,N',N'-tetramethylbutanediamine.

The source of unsaturated aliphatic compounds as the c) ligand must contain C and H, although heteroatoms may also be present in the compound, provided that not more than 1 heteroatom for every 6 carbon atoms are present. Any aliphatic compound containing unsaturation which dissociates from the transition metal centre M at a temperature lower than the temperature at which the b) moiety (Z moiety) dissociates, is a suitable compound for use as a ligand.

The aliphatic unsaturated compound may have from 2 to 32 carbon atoms, preferably from 2 to 8 carbon atoms, more preferably from 2 to 6 carbon atoms. The aliphatic unsaturated compound may be alicyclic or in a linear or branched non-ring structure. Mono- or poly- olefin,

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straight or branched chain compounds are preferred, with mono-olefins being more preferred.

Suitable unsaturated aliphatic compounds as the c) ligand include mono-olefins such as the linear olefins made by the cracking of paraffin wax, commercial olefin products manufactured by ethylene oligomerization are marketed in the United States by Shell Chemical Company under the trademark NEODENE, linear internal olefins made by the chlorination-dehydrochlorination of paraffins, by paraffin dehydrogenation, and by isomerization of alpha-olefins, detergent-range internal or alpha, branched or unbranched, mono-olefins containing from about 8 to about 22 carbon atoms such as those in the carbon number range of C10 to C12, C11 to C15, C12 to C13, and C15 to C18, and ethylene, propylene, 1-butene, 2-butene, 1-pentene, 2-pentene, isopentene, hexene-1, 2-hexene, 3-hexene, 4-methylpentene-1, 2-methylpentene-1, 4-methylbutene-1, 1-heptene, 2-heptene, 3-heptene, 1-octene, 2-octene, 2-methylheptene-1, 4-octene, 3,4-dimethyl-3-hexene, 1-decene, and 1-dodecene, and so forth up to 32 carbon atoms ; dienes and trienes including butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-hexadiene, 1,4-hexadiene, 1,5-hexadiene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, 1,9-decadiene, 1,13-tetradecadiene, 2,6-dimethyl-1,5-heptadiene, 2-methyl-2,7-octadiene, 2,7-dimethyl-2,6-octadiene, 2,3-dimethylbutadiene, ethylidene norbornene, dicyclopentadiene, isoprene, 1,3,7-octatriene, 1,5,9-decartriene, 4-vinylcyclohexene, vinylcyclohexane; divinylbenzene, and cyclic olefins including cyclopentene, cyclobutene, cyclohexene, 3-

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methylcyclohexene, cyclooctene, cyclodecene, cyclododecene, η^5 -cyclohexadienyl, η^6 -cycloheptatriene, η^8 -cyclooctatetracene tetracyclodecene, octacyclodecene, norbornene, 5-methyl-2-norbornene, 5-ethyl-2-norbornene, 5-isobutyl-2-norbornene, 5,6-dimethyl-2-norbornene, 5,5,6-trimethyl-2-norbornene; and acetylenic compounds such as acetylene, methylacetylene, diacetylene, 1,2-dimethylacetylene, η^3 -pentenyl, and norbornadiene.

Sources of the π allyl compound may contain from 3 to 64 carbon atoms. The electronic configuration of the π allyl is not particularly limited, but will generally take on the η^3 state. Any π allyl which dissociates from the transition metal centre at a temperature lower than the temperature at which the b) moiety (Z group) dissociates, is a suitable compound for use as a ligand.

Specific examples of π allyl compounds include allyl acrylate, 2-propen-1-ol, allylamine, allylbromide, allyl hexanoate, allyl cyanide, allyl carbonate, 1-allyl-4-hydroxybenzene, allyl- α -ionone, allyl isocyanate, allyl isothiocyanate, allyl thiol, allyl methacrylate, 4-allyl-2-methoxyphenol, 4-allyl-1,2-methylenedioxybenzene, allyl pelargonate, allyl sulfide, and allyl thioureas.

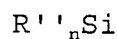
The π -arene compound may contain from 5 to 64 carbon atoms, preferably from 5 to 14 carbon atoms. The electronic configuration of the π allyl and the π -arene compound is not particularly limited, and may take on the η^3 , η^4 , η^5 , η^6 , η^7 , and η^8 states, and may also have any isomeric structure within each η configuration, including the W, U, and S configurations. Any π arene compound, whether substituted, fused, or bridged, which dissociates

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from the transition metal centre at a temperature lower than the temperature at which the b) moiety (Z moiety) dissociates, and which lacks aromatic C-H bonds on the moiety directly bonded to the transition metal, or
 5 contains sterically hindered C-H bonds on the moiety directly bonded to the transition metal, is a suitable compound for use as a ligand. Reference can be had to the Z moiety substituents described above to determine
 10 suitable substituents to sterically hinder the presence of aromatic C-H bonds on the c) ligand.

Suitable π arenes as the c) ligand include tolyl, p-ethylbenzyl, p-isopropylbenzyl, p-propylbenzyl, p-t-butylbenzyl, di-t-butylbenzene, divinylbenzene, p-xylene, 1,3,5-trimethylbenzene (mesitylene), 1,2,4-
 15 trimethylbenzene, 1,3,5-triisopropylbenzene, 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene (durene), pentamethylbenzene, hexamethylbenzene, fluorene, dibenzostannepine, tellurophene, phenothiarisane, selenanthrene,
 20 phenoxaphosphine, phenarsazine, phenatellurazine, 1,2,3,4,4a,9a)-9-(phenylmethylidene)fluorene, and (1,2,3,4,4a,9a)-9-(3-phenyl-2-propenylidene)fluorene.

The source of c) ligand may also comprise compounds derived from polyalkylsilanes. Such silanes can be
 25 represented by the following formula:

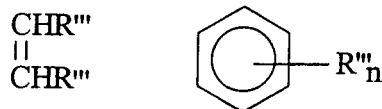


wherein R' is hydrogen, or has the same meaning as R above with respect to suitable phosphine compounds as the c) ligand, and n is an integer ranging from 3-4, provided

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that the silane contains no more than two hydrogen atoms bonded to the silicon atom.

Most preferred examples of the c) ligand are represented by the following structural formulae:



5 wherein each R''' independently represents hydrogen or a saturated or unsaturated, branched or unbranched alkyl, aromatic, alicyclic, or alkaryl group having from 1 to 15 carbon atoms or one or more fused ring structures, more preferably hydrogen or a saturated, branched or
10 unbranched alkyl group having from from 1 to 8 carbon atoms, most preferably from 1 to 4 carbon atoms; and n represents the number of R''' groups and is an integer ranging from 2 to 6. The electronic configuration of the aromatic radical may be in the η^4 , η^5 , or η^6 states.

15 Examples of these most preferred c) ligands include ethylene, propylene, 1-butene, 2-butene, 2-methylpropene-1, 1,4-di-t-butylbenzene, 1,3,5-trimethylbenzene (mesitylene), 1,2,4-trimethylbenzene, 1,3,5-triisopropylbenzene, 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene (durene),
20 pentamethylbenzene, hexamethylbenzene, and di-t-butylbenzene. Among these, ethylene and alkyl substituted C₆ compounds, such as tri-, tetra-, penta-, and hexa- C₁-C₄ alkyl substituted C₆ are particularly
25 suitable.

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While mention has been made of employing c) ligands, any other compound known to act as a ligand may be used in addition to the c) ligand. Examples of additional ligands which may be bonded to the transition metal centre include hydrogen, CO, phosphite, alkoxy, amido, aryloxide, phosphido, arsenic radical, carbonates such as CF_3CO_2^- , sulfonates such as CF_3SO_3^- , and silyl groups.

The total sum of electrons donated by the ligands and the valence electrons possessed by the transition metal is governed by the "eighteen electron rule" in most cases. This rule states that the most stable organometallic compounds tend to be those compounds in which the sum of the electrons donated by the ligands and the metal is eighteen. Those skilled in the art, however, know that there are exceptions to this rule and that organometallic complex compounds having a sum of 16, 17, 19, and 20 electrons are also known. Therefore, organometallic catalysts described herein in which the complexed metal M have a total sum of 16, 17, 18, 19, or 20 electrons in the valence shell and a residual net positive charge of 1, 2 or 3 are included within the scope of the invention.

The catalyst may be synthesized by any of the known literature methods. The halide of the metal-Z moiety can be synthesized by the methods described in C. White, A.Yates, P.M.Maitlis, Inorg. Synth. 1992, V29, 228-234. The catalyst may be manufactured by combining in any sequence, but preferably by combining c) with the reaction product of a) and b).

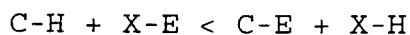
Commercially available Z moiety complexed metals, such as cyclopentadienyl metals, are generally complexed with a ligand other than an olefin or aromatic ligand. A typical ligand in commercially available cyclopentadienyl metal compounds is -CO. Any known method for substituting one ligand for another may be used to prepare the catalyst. The synthesis and purification of the catalyst including the ligands can be performed according to the methods described in T.M.Gilbert, R.G. Bergman, *Inorg. Synth.*, 1990, V.27, 19-22; K.Moseley, J.W. Kang, P.M. Maitlis, *J. Chem.Soc. A*, 1970, 2875-83; W.J.Bowyer, J.W.Merkert, W.E.Geiger, *Organometallics*, 1989, V.8, 191-198; and C.White, P.M. Maitlis, *J.Chem.Soc.A* 1971, 3322-3326. In general, a molar ratio of Z-metal halide salt moieties to the c) ligand compound, as determined by the desired number of ligand compounds bonded to the transition metal, are mixed together in the presence of an optional solvent and acid under heat at -78°C to 100°C for a time sufficient to fully exchange the halide ligands with the c) ligands, after which the product is cooled and the acid removed by distillation under vacuum. The resulting solid may be washed with water and filtered. An aqueous source of a weakly coordinating anion such as NH_4PF_6 is mixed with the filtrate to precipitate the desired product, which may then be washed with more water and dried.

Examples of acids useful as agents to ionically bond the halide to the complex include CF_3COOH , RCOOH , $\text{CF}_3\text{-SO}_3\text{H}$, and other weakly coordinating acids. Examples of other anionic sources useful to precipitate the

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catalyst include NH_4BF_6 , NH_4AsF_6 , NH_4OH , NBa_4PF_6 , and the like.

The functionalizing reagent of the present invention may comprise any group having an electropositive atom capable of bonding to the transition metal centre M and making a strong C-E bond, where E is the electropositive element. The overall reaction is between the reagent containing the electropositive element X-E and the carbon-hydrogen C-H converting to an X-H bond and a carbon-electropositive bond C-E, where X can be hydrogen, another electropositive atom, or other sacrificial portion of the molecule. The electropositive element should be chosen such that the absolute value of the C-H, X-E, C-E, and X-H bond energies satisfy the following equation:



Preferably, the functionalizing reagent comprises a source of boron. The source of boron compounds include numerous boron alkyl, boron aryl, organoboron hydride, or organoboron halide compounds that are known and/or may be prepared in a known manner.

The types of boron compounds and their methods of preparation are described in "Mechanism of the Complexation of Boron Acids with Catechol and Substituted Catechols" by Pizer, R. and Babcock, L., Inorganic Chemistry, vol. 16, No. 7 pp. 1677-1681 (1977); R. K. Boeckman et al. "Catechol boron halides: . . . " Tetrahedron Letter, 1985, 26, pp. 1411-1414; S.Pereira, M.Srebniak, Tetrahedron Lett. 1996, V37, 3283-3286; C.E.

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Tucker, J.Davidson, P.Knochel, J.Org.Chem., 1992, V.57, 3482; R.A. Bowie, O.C. Musgrave, J.Chem.Soc. 1963, 3945-3949; and Herbert C. Brown, "Organic Synthesis via Boranes", John Wiley & Sons, 1975.

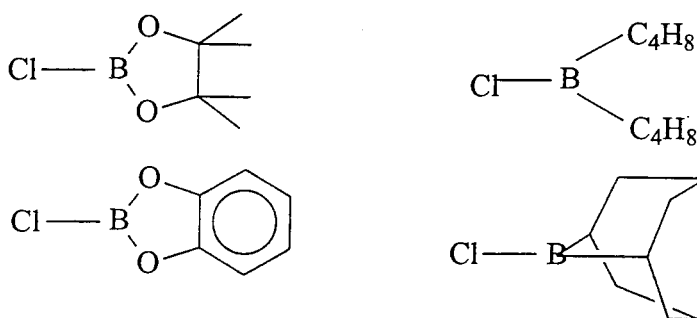
5 Typical representatives of suitable sources of boron compounds are polyalkylmonoboranes and diborane compounds or Lewis base adducts of diborane. Examples of monoboranes include sodium borohydride, potassium borohydride, lithium borohydride, sodium
10 trimethylborohydride, potassium tripropoxy-borohydride, tetramethylammoniumborohydride, triphenylborane, sodium tetraphenylborate, lithium tetraphenylborate, sodium hydrido tris(1-pyrazol)borate, potassium dihydro bis(1-pyrazol)borate, lithium triethylborohydride, lithium tri-
15 sec-butylborohydride, potassium tri-sec-butylborohydride, sodium cyanoborohydride, zinc borohydride, bis(triphenylphosphine) copper (I) borohydride, potassium tetraphenylborate, lithium phenyltriethylborate, lithium phenyltrimethoxyborate, sodium methoxytriphenylborate,
20 sodium diethylaminotriphenylborate, and sodium hydroxytriphenylborate.

In general, boranes derived from olefin hydroboration are useful. These boranes can be triethylborane, dicyclohexylborane, dihexylborane, diethylborane,
25 ethylborane, boron alkyls such as 9-bora-bicyclo-[3.3.1]nonane, diisopinocampheyl borane, dicyclohexyl borane, 2,3-dimethyl-2-butyl borane, 3,5-dimethylborinane and diisoamyl borane, diisopinocampheyl borane, thexylcyclohexyl borane, thexylлимонил borane, and
30 dinorbornylboron.

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Further suitable sources of mono-boranes are reaction products of 1,2-dihydroxybenzenes or 4,6-dimethyl, 1,2-dihydroxybenzenes with boron hydride (boryl catechol or boryl 4,6-dimethylcatechol) and tri-n-butyl boroxine. The boryl compounds in their halogenated state provide a synthetic route to making the functionalizing reagent. Boryl compounds may be reacted in their halo- form with the metal or organo-metallic compounds or complexes. An example of a type of haloboryl compound is the family of halocatecholborane, available commercially. Any halide is suitable, including Cl, Br, and I. The haloboryl compounds in this family may be prepared by reacting an $R(OH)_2$ compound with BX_3 , where X is a halide.

Examples of structures for sources of haloboryl compounds are represented by the following formulae:



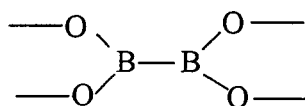
Also suitable as the functionalising agent are borolane, borinane, or diboron compounds.

Bis(dioxaborolane) compounds may be conveniently prepared by reduction of halodiaminoboranes using sodium metal, and subsequent reaction with diols in the presence of acid.

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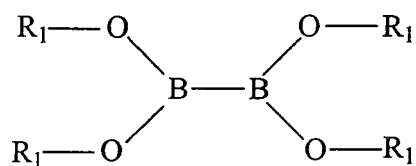
Preferred boron containing functionalizing reagents are the branched or unbranched, substituted or unsubstituted pinacol derivatives of mono- or di- boron. Other examples of diboryl adducts include tetrakis
 5 dimethylaminodiboron, biscatecholate diboron, and substituted bis-catecholate diboron.

Preferred diboryl compounds contain a moiety represented by the following structural formula:



10

In another embodiment, a preferred diboryl functionalizing reagent is represented by the structure:



wherein each R_1 independently represents a linear or
 15 branched, optionally halogen substituted, alkyl group having from 1 to 24 carbon atoms, alkoxy groups containing from 3 to 24 carbon atoms, cycloaliphatic group containing from 3 to 8 carbon atoms, or an aryl group containing from 5 to 16 atoms, and each of the
 20 alkyl, aryl, alkoxy, and cycloaliphatic groups in the aforementioned dioxaborolane compounds may be linear or branched; or substituted with halogens, such as fluorine or bromine, or alkyl groups having from 1 to 16 carbon atoms, preferably from 1 to 4 carbon atoms, and
 25 optionally each R_1 group attached to the same boron atom

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through oxygen atoms may be fused or bridged through any of the aforesaid alkyl, alkoxy, cycloaliphatic or aryl groups.

5 Examples of preferred bis(dioxaborolane) containing compounds include bis-pinacolate diboron and bis(*t*-butylcatecholate) diboron.

The hydrocarbon, preferably an alkane, is selectively functionalized at the primary C-H site by simply combining the catalyst, functionalizing reagent and hydrocarbon under functionalizing reaction conditions. To initiate the reaction by dissociating the ligand from the catalyst, the reaction mixture is heated to any temperature above the temperature at which the catalyst is stored, or room temperature, whichever is less, and below the thermal decomposition temperature of the catalyst or functionalizing reagent. It is desirable that the reagent species employed activates at temperatures above those the reagent would encounter during shipping or storage to ensure storage stability. Accordingly, suitable reaction temperatures range from 70°C to 250°C, more preferably from 100°C to 200°C.

While the molar ratio of ingredients is not critical, it is desirable to use a stoichiometric excess of functionalizing reagent over the metal catalyst (>1:1), and preferably a molar ratio of >10:1, and more preferably >100:1, and most preferably >200:1, respectively. The amount of catalyst is also not particularly limited. However, an amount of catalyst ranging from 0.1 to 10 mole%, preferably from 0.1 to 5 mole%, based on the the combined moles of catalyst and

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hydrocarbon will operate to functionalize the hydrocarbon at the primary C-H site. Other reaction conditions are not particularly limited.

5 The reaction time is not limited, other than the reaction time should be as short as possible to reduce cycle time and increase throughput. Reaction times may range from 0.5 hours to 48 hours. The reaction may be carried out at any desired pressure. Pressures within the range of 0 to 0.69 MPa (0 to 100 p.s.i.g.) are
10 suitable.

The reaction between the functionalizing reagent and the hydrocarbon in the presence of the catalyst may be carried out in any solvent for both the reagent and hydrocarbon. The process of the invention advantageously
15 employs the hydrocarbon as the solvent for the functionalizing reagent without need to add additional solvent.

In a preferred embodiment, the catalyst is soluble in the hydrocarbon, said hydrocarbon conveniently comprising
20 an alkane.

Once the reaction is complete, the functionalized hydrocarbon may be separated and isolated from the reaction mixture by distillation, chromatography, or crystallization.

25 The process of the invention is 80% or more selective toward functionalizing a primary C-H bond on hydrocarbon molecules, in contrast to a secondary C-H bonding site. Of the C-H sites on the hydrocarbon which are converted, the process of the invention is capable of selectively
30 functionalizing 90% or more, preferably 95% or more, and

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more preferably 98% or more, and most preferably 99% or more of the converted C-H sites on the hydrocarbon at the primary C-H site.

5 The process is also catalytic. The process of the invention enables one to thermally activate the catalyst while achieving 50 or more turnovers. The number of catalyst turnovers is calculated by dividing the moles of product made by the moles of catalyst added to the process. Preferably, the catalyst turns over more than 10 75 times, more preferably 100 times or more.

In another embodiment, there is provided a catalytic process having more than 50 turnovers comprising thermally activating said catalyst in the presence of a functionalizing reagent and an aliphatic hydrocarbon or 15 alkyl branched alicyclic hydrocarbon containing primary C-H bonds, said catalyst comprising:

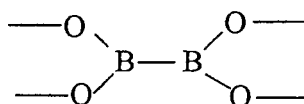
- a) a source of a transition metal;
- b) a source of a 3 to 8, cyclic or non-cyclic, aromatic or non-aromatic, neutral, cationic or 20 anionic, substituted or unsubstituted, electron donor moiety which does not dissociate under thermal reaction conditions, wherein said moiety
 - (i) lacks aromatic C-H bonds on the moiety directly bonded to the transition metal, or
 - 25 (ii) contains sterically hindered aromatic C-H bonds on the moiety directly bonded to the transition metal; and
- c) a source of ligands capable of formally donating an electron pair to the transition metal of a) and 30 which dissociate thermally;

- 40 -

and wherein said functionalizing reagent comprises a source of B, C, N, O, Si, P, S, Ge, As, Al, or Se.

In yet another embodiment of the invention, there is provided a functionalization process comprising
5 selectively functionalizing 80% or more of primary C-H hydrocarbon bonds in a hydrocarbon composition in the presence of a thermally activated catalyst, wherein said process turns over the catalyst 50 or more times.

There is further provided a functionalization process
10 comprising selectively functionalizing 80% or more of primary C-H hydrocarbon bonds in a hydrocarbon composition in the presence of a thermally activated catalyst and a functionalizing reagent, wherein said functionalizing reagent comprises a compound containing a
15 moiety represented by the following structure:



Without being bound to a theory, and for illustration purposes only, it is believed that one possible mechanism for the functionalization of the hydrocarbon, using B_2pin_2 and a $\text{Cp}^*\text{Rh}(\text{C}_2\text{H}_2)_2$ ($\text{Cp}^* = \eta^5 \text{C}_5\text{Me}_5$) and nonane as
20 illustrative examples of the functionalizing reagent, catalyst, and hydrocarbon, respectively, proceeds according to the following catalytic cycles shown in the accompanying figures, wherein:-

Figure 1 shows the first stage with B_2pin_2 as reagent;
25 and

Figure 2 shows the second stage with HBpin as reagent.

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Once the hydrocarbon is functionalized as a boryl adduct of the hydrocarbon at a primary C-H site, the adduct may be converted into any other hydrocarbyl containing functional group using well known and conventional processes, such as those described in H.C. Brown, "Hydroboration," 1962; R.C. Larock, "Comprehensive Organic Transformations; A Guide To Functional Group Preparations," New York, New York, 1989; and H.C. Brown, "Organic Synthesis via Boranes," New York, New York, 1975. For example, primary alcohols can be manufactured by the oxidation of the primary alkylboryl adduct using an alkali metal hydroxide solution in the presence of a peroxide, or the adducts may be carbonylated to an alcohol by reacting the primary alkylboryl adduct in the presence of carbon monoxide, water and an alkali metal hydroxide such as NaOH or KOH.

Carboxylic acids can be prepared by oxidation of the borane functionalized hydrocarbon to an alcohol, followed by conventional oxidation of the alcohol to the acid. Amine functional hydrocarbons can be prepared by reaction of borane functionalized hydrocarbon with o-hydroxylamine sulfonic acid and chloroamine"

The functionalized borane hydrocarbons converted to -OH, -COOH, and -NH₂ or -NHR bearing compounds may be further converted to hydrocarbons containing ester, amide, imide, carbonate and polycarbonate, sulfonate, ether, polyether, and glycidyl ether groups.

The present invention will now be illustrated by the following examples which are not intended to limit the scope of the invention in any way.

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Examples

Unless otherwise noted, all manipulations were carried out in an inert atmosphere glovebox or by using standard Schlenk line techniques. Solids were handled in a Vacuum Atmospheres drybox under nitrogen. All solvents were dried over appropriate reagents and distilled under nitrogen before use. ^1H NMR and ^{13}C NMR spectra were recorded on either a General Electric QE-300 or Bruker AM-500 NMR spectrometer, and ^{11}B and $^{31}\text{P}(\text{H})$ NMR spectra were recorded on an Omega 300 NMR spectrometer. ^{11}B and $^{31}\text{P}(\text{H})$ chemical shifts are reported in ppm relative to external standards of BF_3 , Et_2O and 85% H_3PO_4 , respectively. Proton chemical shifts are reported in ppm relative to residual protiated solvent as internal standard. Elemental analysis were performed by Atlantic Microlabs, Inc., of Norcross, GA. Octane, decan, methylcyclohexane and benzene were distilled from sodium/benzophenone ketyl prior to use. Benzene D_6 was dried over sodium/benzophenone ketyl and degassed before use. B_2pin_2 and HBpin were purchased from Frontier Science or Aldrich and were used as received. 1-Octene, 1-decene, ethylene, trimethylborate, triethylsilane, vinyltrimethylsilane, anhydrous n-butyl ether, and dodecahydrotriphenylene were purchased from Aldrich and were used as received without further purification. The metal compounds $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{IrCl}_3 \cdot \text{H}_2\text{O}$ were obtained from Johnson-Matthey.

^{31}P NMR was operating at 121 MHz, and ^1H NMR was operating at 300 or 500 Hz. ^{11}B NMR was operating at

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96.4 MHz. All ^{31}P NMR spectra were proton-decoupled. Integration of the ^{31}P resonances were carried out on spectra that were acquired with gated decoupling and 10 second delay times between acquisition pulse sequences. 5 ^1H chemical shifts were measured relative to partially deuterated solvent peaks.

Catalyst Precursor Example 1

This example illustrates the synthesis of one embodiment of the catalyst precursor used to make a catalyst within the scope of the invention. 10

$[\text{C}_5\text{Me}_5\text{RhCl}_2]_2$ was synthesized according to the following procedure: A solution of 0.0042 moles of rhodium trichloride hydrate commercially available from Strem Chemicals and 0.007 moles of 15 pentamethylecyclopentadiene commercially available from Aldrich in 40 ml methanol was refluxed under nitrogen for 48 hours with stirring. This procedure is described in C. White, A.Yates, P.M Matilis, Inorg.Synth. 29, 228-234 (1992), the contents of which are incorporated herein by reference. 20 $[\text{C}_5\text{Me}_5\text{RhCl}_2]_2$ precipitated out of solution. It was collected and purified by recrystallization in a chloroform/hexane. The yield was 0.93 grams.

Catalyst Precursor Example 2

This example illustrates that synthesis of another embodiment of the catalyst precursor to make a catalyst within the scope of the invention. 25

$[\text{C}_5\text{Me}_5\text{IrCl}_2]_2$ was synthesized according to the following procedure: A solution of about 0.0058 moles of iridium trichloride hydrate commercially available from

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Strem Chemicals and 0.0085 moles of pentamethylcyclopentadiene commercially available from Aldrich in 40 ml methanol was refluxed under nitrogen for 48 hours with stirring. The $[\text{C}_5\text{Me}_5\text{IrCl}_2]_2$ product precipitated out of solution. It was collected and purified by recrystallization from chloroform/hexane. The yield was 1.05 grams.

Catalyst Example 3

This example illustrates that synthesis of another embodiment of the catalyst within the scope of the invention.

$\text{C}_5\text{Me}_5\text{IrH}_4$ was synthesized according to the following procedure: Air stable $[\text{Ir}(\text{C}_5\text{Me}_5)]_2(\text{M}-\text{H})_3[\text{PF}_6]$, wherein M is the bridging ligand, was prepared by bubbling hydrogen gas through a solution of 0.000834 moles of $[\text{C}_5\text{Me}_5\text{IrCl}_2]_2$ in a mixture of 2-propanol, acetone, and water in a volume ratio of 2:2:1. The resulting $[\text{Ir}(\text{C}_5\text{Me}_5)]_2(\text{NH})_3[\text{PF}_6]$ product was isolated by filtration, evaporation of acetone and isopropanol and treatment with an aqueous solution of 0.001 mol NH_4PF_6 in 3 mL of water. $[\text{Ir}(\text{C}_5\text{Me}_5)]_2(\text{NH})_3[\text{PF}_6]$ was collected by filtration and purified by crystallization from CHCl_3 and heptane. 200 mg, or 0.249 mmol of the $[\text{Ir}(\text{C}_5\text{Me}_5)]_2(\text{NH})_3[\text{PF}_6]$ product was slurried in hexane, cooled to about -40°C , after which a 1.5 mmol of $\text{Li}[\text{BET}_3\text{H}]$ in 2 mL of toluene was added by pipette to the cooled slurry in an inert atmosphere glovebox. The resulting $\text{C}_5\text{Me}_5\text{IrH}_4$ product was isolated by filtering the slurry through an alumina column, followed by removal of

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the solvent through by evaporation under vacuum. 128 mg of the crude catalyst product was purified by sublimation at 30-40 °C and 2.67 Pa (20 mtorr). The procedure for synthesis of this catalyst is also explained in Gilbert,
5 R.G. Bergman, Inorg. Synth. 27, 19-22 (1990).

The yield of the $(\eta^5\text{C}_5\text{Me}_5)\text{IrH}_4$ catalyst product was 36% (59 mg., 0.18 mmol). The spectroscopic characterization was as follows: $^1\text{HNMR}$ (C_6D_6): δ 1.99 (s, 15H), -15.4 (s. 4H).

10 Catalyst Example 4

This example illustrates that synthesis of another embodiment of the catalyst within the scope of the invention.

$\text{C}_5\text{Me}_5\text{Ir}(\text{ethylene})_2$ was synthesized according to the
15 following procedure: Ethylene was bubbled into a suspension of 240 mg, or 0.301 mmol, of $[\text{C}_5\text{Me}_5\text{IrCl}_2]_2$ in anhydrous sodium carbonate in ethanol under a nitrogen pad at 70°C for 3 hours. The crude products were obtained by filtration and the removal of the solvent by
20 evaporation. The crude catalyst was sublimed at 25°C at 0.67 Pa (5 mtorr) to purify. The procedure for the synthesis of this catalyst is described in K. Moseley, J.W. Kang, P.M. Matilis, J. Chem. Soc A, 2875-83 (1970), the contents of which are incorporated herein by
25 reference.

The yield of the $\text{C}_5\text{Me}_5\text{Ir}(\text{ethylene})_2$ catalyst product was 82% (189mg., 0.492 mmol). The spectroscopic characterization was as follows: $^1\text{HNMR}$ (C_6D_6): δ 1.78 (m, 4H), 1.56 (s. 15H), 1.14 (m, 4H).

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Catalyst Example 5

This example illustrates that synthesis of another embodiment of the catalyst within the scope of the invention.

5 $C_5Me_5Rh(ethylene)_2$ was synthesized according to the following procedure: Ethylene was bubbled into a suspension of 240 mg, or 0.324 mmol, of $[C_5Me_5RhCl_2]_2$ in anhydrous sodium carbonate in ethanol under a nitrogen pad at 70°C for 3 hours. The crude products was obtained
10 by filtration and the removal of the solvent by evaporation. The crude catalyst was sublimed at 25°C at 0.67 Pa (5 mtorr) to purify. The procedure for the synthesis of this catalyst is described in K. Moseley, J.W. Kang, P.M. Matilis, J. Chem. Soc A, 2875-83 (1970),
15 the contents of which are incorporated herein by reference.

The yield of the $\eta^5-C_5Me_5Rh(ethylene)_2$ catalyst product was 41% (79mg., 0.267mmol). The spectroscopic characterization was as follows: 1HNMR (C_6D_6): δ 1.96
20 (m, 4H), 1.58 (s, 15H), 1.51 (m, 4H).

Catalyst Example 6

This example illustrates that synthesis of another embodiment of the catalyst within the scope of the invention.

25 $C_5Me_5Rh(C_2H_3SiMe_3)_2$ was synthesized according to the following procedure: $[C_5Me_5IrCl_2]_2$ was reduced by zinc powder 411 mg in the presence of 489 mg, 4.8 mmol, vinyltrimethylsilane in a solution of tetrahydrofuran at 20°C for 12 hours. The product obtained was isolated by

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filtration and the removal of solvents by evaporation. The procedure for the synthesis of this catalyst is described in K. Moseley, J.W. Kang, P.M. Matilis, J. Chem. Soc A, 2875-83 (1970), the contents of which are
5 incorporated herein by reference.

The yield of the $[\text{C}_5\text{Me}_5\text{Rh}(\text{C}_2\text{H}_3\text{SiMe}_3)_2$ catalyst product was 82% (143 mg., 0.326 mmol). The spectroscopic characterization was as follows: $^1\text{HNMR}$ (C_6D_6): δ 2.2 (dd, $J=11.0$, 2.3 2H), (s. 15H), 1.50 (s, 15H), 1.22 (m, 4H),
10 0.28 (s, 18H).

Catalyst Example 7

This example illustrates that synthesis of another catalyst.

$\eta^5\text{-C}_5\text{Me}_5\text{RhH}_2(\text{SiEt}_3)_2$ was synthesized according to the
15 following procedure: 167 mg, 0.210 mmol of $[\text{C}_5\text{Me}_5\text{RhCl}_2]_2$ was combined with 820 mg., 7.05 mmol, triethylsilane under stirring in dry toluene for 8 hours at 60°C and then 3 days at 20°C. The crude product was isolated by the removal of the solvent on a rotary evaporator. The
20 product was purified by extraction with hexane, followed by chromatography on Florosil. The procedure for the synthesis of this catalyst is described in M.J. Fernandez, et al., J.Am.Chem.Soc. 106, 5458-5463 (1984) the contents of which are incorporate herein by
25 reference. The yield of the $\eta^5\text{-C}_5\text{Me}_5\text{RhH}_2(\text{SiEt}_3)_2$ catalyst product was 68% (172 mg., 0.365 mmol). The spectroscopic characterization was as follows: $^1\text{HNMR}$ (C_6D_6): δ 1.7 (s, 15H), 1.09 (t, $J=7.2$ Hz, 18H), 0.89 (q, $J=7.2$ Hz, 12H).

Catalyst Example 8

This example illustrates the synthesis of another embodiment of the catalyst within the scope of the invention.

5 $[(\eta^6\text{-C}_6\text{Me}_6)\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)](\text{PF}_6)$ catalyst precursor was synthesized according to the following procedure:

Following preparation of the $[\text{C}_5\text{Me}_5\text{RhCl}_2]_2$ intermediate as described in Example 1, 195 mg, or 0.316 mmol, of $[\text{C}_5\text{Me}_5\text{RhCl}_2]_2$ and 233 g, or 1.38 mmol, of

10 hexamethylbenzene was combined with 4.5 ml of trifluoroacetic acid. The mixture was refluxed for 7 hours and then cooled to room temperature.

Trifluoroacetic acid was removed under vacuum. The resulting white solid was dissolved in 12 mL of water.

15 The slurry was filtered through a medium fritted funnel.

An aqueous solution of NH_4PF_6 (345 mg., 2.12 mmol) was added to the filtrate to precipitate the catalyst as an off white solid. The solid was collected by filtration and washed with water (3X7 ml) and Et_2O (3X7 ml). The

20 solid was dried under high vacuum and 100°C for 2 hours.

$[(\eta^4\text{-C}_6\text{Me}_6)\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)]$ was synthesized according to the following procedure: 505 mg, 0.731 mmol, of

$[(\eta^6\text{-C}_6\text{Me}_6)\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)](\text{PF}_6)$ was reduced by combining it with 250 mg, 132 mmol, dicyclopentadienyl cobalt in
25 pentane at room temperature for allowing the stir for 9 hours. The product was isolated by filtration, followed by removal of pentane by evaporation under vacuum.

The yield of the $[(\eta^6\text{-C}_6\text{Me}_6)\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)]$ catalyst product was 96% (255 mg., 0.637 mmol). The spectroscopic

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characterization was as follows: ^1H NMR (C_6D_6): δ 2.05 (s, 6H), 1.64 (s, 15H), 1.42 (s, 6H), and 1.28 (s, 6H).

Organoborane Example 9

2-octyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared by placing 272 mg, or 2.42 mmol, of 1-octene and 137 mg, or 1.07 mmol, of pinacolborane into an NMR sample tube. The solution was frozen, the system was evacuated under high vacuum, and the sample tube was flame-sealed. The sample was then heated at 120°C for 14 hours. The reaction vessel was opened in a dry box, and the reaction mixture was passed through a small plug of silica suspended in pentane. The solvent was evaporated under vacuum, providing 2-octyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as a clear oil. The yield was 83% (213 mg, 0.885 mmol). This sample was prepared as a reference standard to detect the presence of internal isomers in a functionalization reaction where selectivity towards the primary C-H bond site on the hydrocarbon (octane) is desired. This product was characterized by GC/MS, ^1H and ^{11}B NMR.

Organoborane Example 10

2-decyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared in the same way as in Example 10, except that 1-octene was replaced with 1-decyl, to produce a product yield of 70%.

This sample was prepared as a reference standard to detect the presence of internal isomers in a functionalization reaction where selectivity towards the primary C-H bond site on the hydrocarbon (decane) is

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desired. This product was characterized by GC/MS, ^1H and ^{11}B NMR.

Organoborane Example 11

2-(1-methyl-heptyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared in situ by reacting 2.5 g (12.9 mmol) of 2-bromooctane and 0.756 g (31.1 mmol) Mg turnings in anhydrous 10 ml THF at 22°C. The solution was transferred slowly by cannula into a diethyl ether solution of 1.42 g (13.7 mmol) $\text{B}(\text{OMe})_3$, with stirring at -72°C under nitrogen. The solution was reacted at this temperature for 4 hours and was then gradually warmed to room temperature. To the solution was added 10 mL water containing (1.0 mL) H_2SO_4 . The resulting solution was stirred for 1 hours. The ether layer of the mixture was separated, and the solvent was evaporated under vacuum to provide 894 mg of a white solid.

Without further purification, 553 mg of the crude 2-octylboronic acid was combined with 430 mg of pinacol in THF. The reaction solution was heated at reflux for two days, after which time the solvent was evaporated under vacuum. The resulting crude product was purified by silica gel chromatography, providing a clear oil. The yield of 2-(1-methyl-heptyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was 22% (426 mg, 1.77 mmol) with respect to 2-bromooctane.

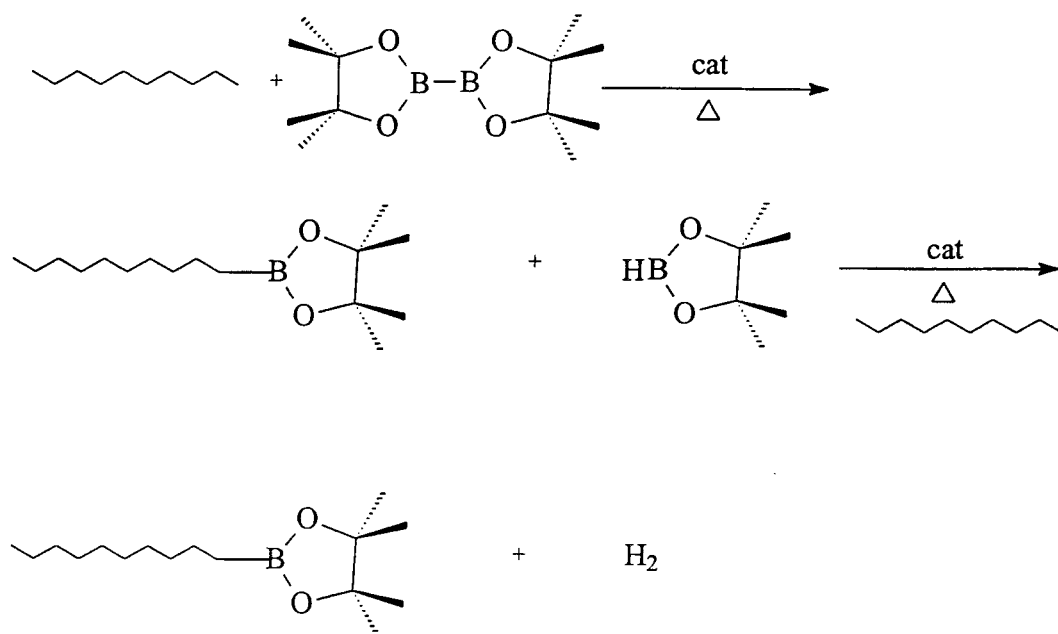
This sample was prepared as a reference standard to detect the presence of internal isomers in a functionalization reaction where selectivity towards the primary C-H bond site on the hydrocarbon (octane) is

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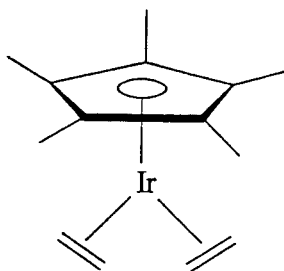
desired. This product was characterized by GC/MS, ^1H and $^{11}\text{BNMR}$, $^{13}\text{CNMR}$, and High Resolution Mass Spectroscopy.

Functionalization Example 12

A commercially available functionalizing reagent
 5 4,4,5,5-tetramethyl-1,3,2-dioxaborolane was reacted with
 n-decane in the presence of the $\eta^5\text{-C}_5\text{Me}_5\text{Ir(ethylene)}_2$
 catalyst as prepared in Example 4 to produce a
 functionalized decylboryl adduct according to the
 following equation:



cat=



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In a dry box, a solution containing 0.0151 mmol of the $\text{Cp}^*\text{Ir}(\text{C}_2\text{H}_5)_2$ ($\text{Cp}^* = \eta^5\text{C}_5\text{Me}_5$) catalyst and 33.6 mg (0.132 mmol) B_2pin_2 ($\text{B}_2\text{pin}_2 = 4,4,5,5\text{-tetramethyl-1,3,2-dioxaborolane}$) obtained from Callery Chemicals in 0.7 ml of dry n-decane was placed in an NMR sample tube attached to a Kontes vacuum adapter using a Cajon Ultratorr connector. The solution was frozen, and the system was evacuated under high vacuum. The sample tube was then flame sealed. The sample was removed from the box and placed in a 190°C oil bath. The solution was heated for 130 hours at 190°C and monitored periodically by ^{11}B NMR spectroscopy. ^{11}B NMR spectroscopy showed that B_2pin_2 was completely consumed and that HBpin was formed as accompanying product.

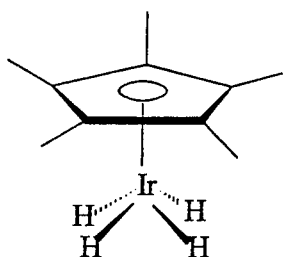
The HBpin sample was then heated at 210°C for 115 hours, after which time the ^{11}B NMR spectrometer showed complete consumption of pinacolborane. The sample was brought into the dry box and a solution of dodecahydrotriphenylene (15.2 mg, 0.0632 mmol) in benzene was added. An aliquot was then removed and analyzed by GC. The yield of the 1-decylBpin functionalized product was 46%. 100% of the B_2pin_2 was reacted. 98% of the HBpin was reacted. The catalyst turnover count was 8. The reaction proceeded slowly as indicated by the amount of time taken to substantially completely convert the B_2pin_2 functionalizing reagent. Characterization of the 1-decylBpin product by GC/MS and ^1H NMR revealed functionalization at the primary and terminal C-H bond of decane. The selectivity toward the 1-decylBpin product

at the primary C-H bond was exclusive, on the order of 99.9%+. Other decyl by-products were not detected.

Comparative Functionalization Example 12

5 The same reactants and reaction conditions as used in Example 12 were followed in this comparison example, with the following differences:

The catalyst employed did not contain an unsaturated aliphatic ligand or a π arene ligand. Instead, the catalyst used was the η^5 -C₅Me₅IrH₄ catalyst compound
10 obtained in Catalyst Example 3, having the following structure:

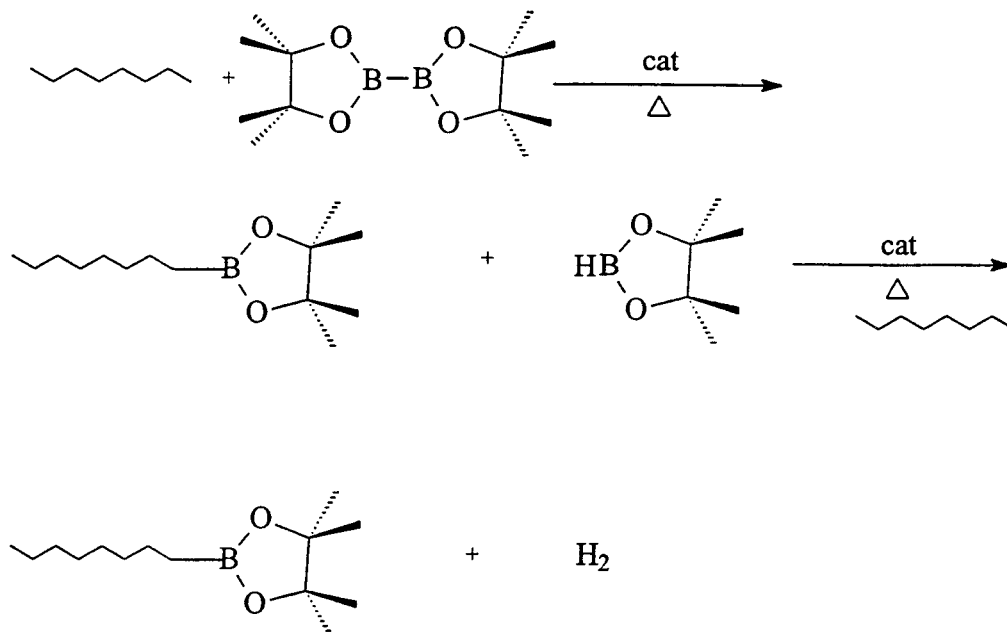


The amount of catalyst employed was 10%, and the reaction mixture was reacted at 170°C. After 4 days, the
15 yield of 1-decylBpin was only 16%, indicating low catalytic activity. It is believed that hydrogen does not readily dissociate from the metal centre by application of thermal energy, thereby rendering this compound unsuitable as a catalyst for use in a thermal
20 process.

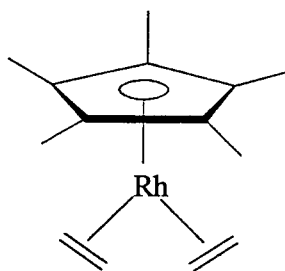
Functionalization Example 13

The functionalizing reagent 4,4,5,5-tetramethyl-1,3,2-dioxaborolane obtained from Callery Chemicals was reacted with n-octane in the presence of
25 C₅Me₅Rh(ethylene)₂ catalyst as prepared in Example 5 to

produce a functionalized decylboryl adduct according to the following equation:



cat=



5

In a dry box, a solution containing 0.00125 mmol of the $\text{Cp}^*\text{Rh}(\text{C}_2\text{H}_2)_2$ ($\text{Cp}^* = \eta^5\text{C}_5\text{Me}_5$) catalyst and 31.7 mg (0.125 mmol) B_2pin_2 ($\text{B}_2\text{pin}_2 = 4,4,5,5\text{-tetramethyl-1,3,2-dioxaborolane}$) obtained from Callery Chemicals in 0.7 ml of dry n-octane was placed in a screw-cap NMR sample tube and sealed tightly. The sample was removed from the box

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and placed in a 150°C oil bath. The solution was heated for 80 hours at 150°C and monitored periodically by ^{11}B NMR spectroscopy. ^{11}B NMR spectroscopy showed that HBpin was completely consumed.

5 The sample was brought into the dry box and a solution of dodecahydrotriphenylene (15.2 mg, 0.0632 mmol) in benzene was added by pipette. An aliquot was then removed and analyzed by GC.

10 The yield of the 1-octylBpin functionalized product was 72%. 100% of the B_2pin_2 was reacted. The catalyst turnover count was 144. The amount of time taken to convert B_2pin_2 was 80 minutes. Characterization of the 1-octylBpin product by GC/MS and ^1H NMR revealed functionalization at the primary and terminal C-H bond of octane. The selectivity toward the 1-octylBpin product at the primary C-H bond was exclusive, 99.9+%. Other octyl by-products were not detected.

Functionalization Examples 14-20

20 The same procedures as set forth in Example 13 was followed in Examples 14-22, except the amounts and type of catalyst, type of hydrocarbon substrate, and time of reaction were varied as set forth in Table 1 below. The catalyst turnover and selectivity to the primary C-H bond position on the hydrocarbon substrate results are also set forth in Table 1. Conversion of B_2pin_2 in each case was 100%, except in Example 19, which was 99%. Yields were determined by GC. When benzene was used as the substrate, a solution containing the catalyst was heated at 150°C, and a known amount of dodecahydrotriphenylene was added as an internal standard before or after the

25

30

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reaction. In each example, B₂pin₂ was used as the functionalizing reagent in the amounts specified in Examples 12-13.

Table 1

Example	Hydrocarbon Substrate	Catalyst Example #	Cat. Loading (mole)	Time (h)	Yield of Rbpin (%)	Catalyst Turnover	Selectivity (%)
14	n-octane	5	5%	5	84	34	100
15	n-octane	7	5%	90	39	16	100
16	n-octane	8	5%	25	88	35	100
17	n-octane	8	1%	80	72	144	100
18	n-octane	6	5%	27	53	21	100
19	n-butyl ether	8	4%	80	64	32	100
20*	2-methyl heptane	8	1%	60	61	122	100
21	2-methyl heptane	5	2.5%	30	73	58	Same as Ex. 20

*2-Methylheptane possesses two types of primary C-H bonds. The reaction leads to preferential reaction at the less hindered methyl group to provide a 5:1 ratio of the two terminal functionalization products.

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In Example 14, reaction of octane with B₂pin₂ at 150°C for 50 minutes gave complete conversion of B₂pin₂ to octylBpin and HBpin. In this case, the yield of octylBpin was higher than the amount of converted diboron reagent, suggesting that the reaction of HBpin with octane was also occurring, but at a slower rate than the reaction of B₂pin₂. Upon further heating the reaction solution at the same temperature for 5 hours total, HBpin was completely consumed. Analysis of the borane products by GC/MS showed that 1-octylBpin was the only isomer formed by this process. Comparison of the GC/MS of this product with the GC/MS of 2-octylBpin prepared in Example 10 revealed that no 2-octylBpin internal isomer was made as a by-product. Other ethylene-boryl by-products derived from the ethylene ligand were detected by GC/MS. Example 16 employed the catalyst from Example 7 containing (HSiEt₃)ligands. The reaction rate, however, was slower than that for Example 15, and the yields were unsatisfactory.

The functionalization of n-octane in Example 16, using the aromatic η^4 -C₆Me₆ ligand on the catalyst, proceeded selectively to the terminal 1-octylBpin product in high yield, at a reaction rate intermediate to the rate in Examples 14 and 15. ¹¹BNMR spectrometry showed clean conversion of B₂pin₂ to the 1-octylBpin and HBpin within 1 hour. Within 25 hours, the HBpin was completely converted to the 1-octylBpin.

The yield and selectivity in Examples 20 and 21 were based on functionalization at the primary C-H bond site

on the methyl branch of the methylcyclohexane substrate. Example 19 is shown to demonstrate that a hydrocarbon containing a heteroatom, oxygen, may be selectively and thermally functionalized at a primary C-H bond.

C L A I M S

1. A process for selectively functionalizing an aliphatic hydrocarbon and/or alkyl branched alicyclic hydrocarbon at a primary C-H hydrocarbon bond comprising thermally reacting a functionalizing reagent and the hydrocarbon in the presence of a catalyst, said catalyst comprising:
- 5
- a) a source of a transition metal;
- 10 b) a source of a 3 to 8, cyclic or non-cyclic, aromatic or non-aromatic, neutral, cationic or anionic, substituted or unsubstituted, electron donor moiety which does not dissociate under thermal reaction conditions, wherein said moiety
- 15 (i) lacks aromatic C-H bonds on the moiety directly bonded to the transition metal, or
- (ii) contains sterically hindered aromatic C-H bonds on the moiety directly bonded to the transition metal; and
- 20 c) a source of ligands capable of formally donating an electron pair to the transition metal of a) and which dissociate thermally;
- and wherein said functionalizing reagent comprises a source of boron.
- 25 2. The process of claim 1, wherein the selectivity to functionalizing the hydrocarbon at a primary C-H bond is 80% or more, in contrast to a secondary C-H bonding site.

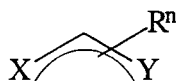
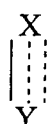
- 61 -

3. The process of claim 1 or 2, wherein the transition metal comprises Rh, and the aliphatic hydrocarbon comprises an alkane.

4. The process of any one of claims 1 to 3, wherein the
5 b) moiety comprises a fully substituted η^5 cyclopentadienyl moiety.

5. The process of any one of claims 1 to 4, wherein the
b) moiety contains no aromatic C-H bonds.

6. The process of any one of claims 1 to 5, wherein the
10 c) ligand is represented by any one of the following structural formulae:



wherein X and Y each independently represent one or more
of H, C, B, S, N, Si, Sn, P, and As, and combinations
15 thereof, to which saturated or unsaturated, branched or
unbranched alkyl, aromatic, alicyclic, or alkaryl groups
may be bonded, and wherein X and Y may be bridged to form
a cyclic arene compound which may contain branches,
substituents, or fused aromatic rings, R represents
20 hydrogen or one or more optional branches or
substituents, and n represents an integer ranging from 0
to 8.

7. The process of any one of claims 1 to 6, wherein the
c) ligand comprises a linear or branched aliphatic
25 olefinic group having from 2 to 8 carbon atoms.

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8. The process of any one of claims 1 to 7, wherein said functionalizing reagent comprises a source of boron alkyl, boron aryl, organoboron hydride, or organoboron halide compounds.

5 9. The process of any one of claims 1 to 8, wherein the functionalizing reagent and the hydrocarbon are reacted in the presence of said catalyst at a temperature ranging from 70°C to 250°C.

10 10. The process of any one of claims 1 to 9, wherein the molar ratio of functionalizing reagent to catalyst is greater than 10:1.