

SYNTHESIS AND HYDROGENATION OF METATHESIS DIMERS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 63/425,964, filed on November 16, 2022, which is incorporated by reference herein in its entirety.

TECHNICAL FIELD

[0002] This disclosure relates to methods of synthesizing cyclic alkanes, wherein cyclic alkene dimers are formed using a metathesis catalyst, followed by hydrogenation of said cyclic alkene dimers to yield cyclic alkanes.

BACKGROUND

[0003] The development of weapons and vehicles that can travel at hypersonic speeds is becoming increasingly prevalent. Currently, the cooling capacity of kerosene-based fuels is relatively low even with endothermic cracking reactions, and this limits the Mach number that can be achieved. Moreover, increasing the fuel cooling capacity by allowing the fuel to reach higher temperatures is not feasible because coke formation could lead to heat exchanger failure.

SUMMARY

[0004] This disclosure describes metathesis reactions between various olefins, including commodity alkenes, and hydrogenation of the resulting products unlock the production of cyclic or linear alkanes not selectively accessible by other organic transformations. The resulting products can be endothermic fuels which have the potential to be used as fuel components for hypersonic applications.

[0005] Provided herein are methods of synthesizing a cyclic alkane. The methods include contacting one or more C_3 - C_{20} alkenes with a metathesis catalyst, wherein the contacting occurs under conditions suitable to yield a cyclic alkene dimer and at least one C_3 - C_{20} alkene is a cyclic alkene; and hydrogenating the cyclic alkene dimer to yield an alkane dimer, wherein the alkane dimer is a cyclic alkane.

[0006] The details of one or more embodiments of the subject matter of this disclosure are set forth in the accompanying drawings and the description. Other features, aspects, and

advantages of the subject matter will become apparent from the description, the drawings, and the claims.

BRIEF DESCRIPTION OF DRAWINGS

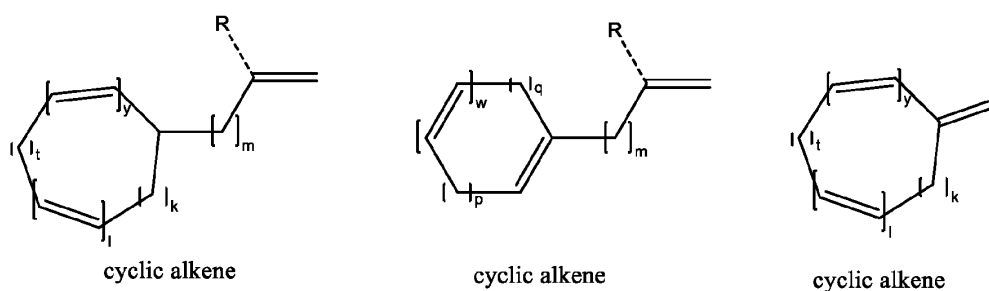
- [0007] FIG. 1 is a non-limiting scheme of metathesis of alkenes and hydrogenation thereof using the methods of the disclosure.
- [0008] FIG. 2 is a gas chromatography (GC) spectrum of the products from a metathesis homodimerization of 4-vinylcyclohexene using the methods of the disclosure.
- [0009] FIG. 3 is a GC spectrum of the products from the hydrogenation of the metathesis dimer of 4-vinylcyclohexene using the methods of the disclosure.
- [0010] FIG. 4 is a series of GC spectra of the products from the metathesis heterodimerization of 1-octene and beta-pinene using the methods of the disclosure, wherein A is the reaction mixture, B is the 1st fraction, C is the 2nd fraction, and D is the 3rd fraction.
- [0011] FIG. 5 is a GC spectrum of the products from the hydrogenation of metathesis pinene-octene dimers using the methods of the disclosure.
- [0012] FIG. 6 is a GC spectrum of the products from the metathesis homodimerization of vinylcyclobutane using the methods of the disclosure.
- [0013] FIG. 7 is a GC spectrum of the products from the hydrogenation of 1,2-dicyclobutylethene using the methods of the disclosure.

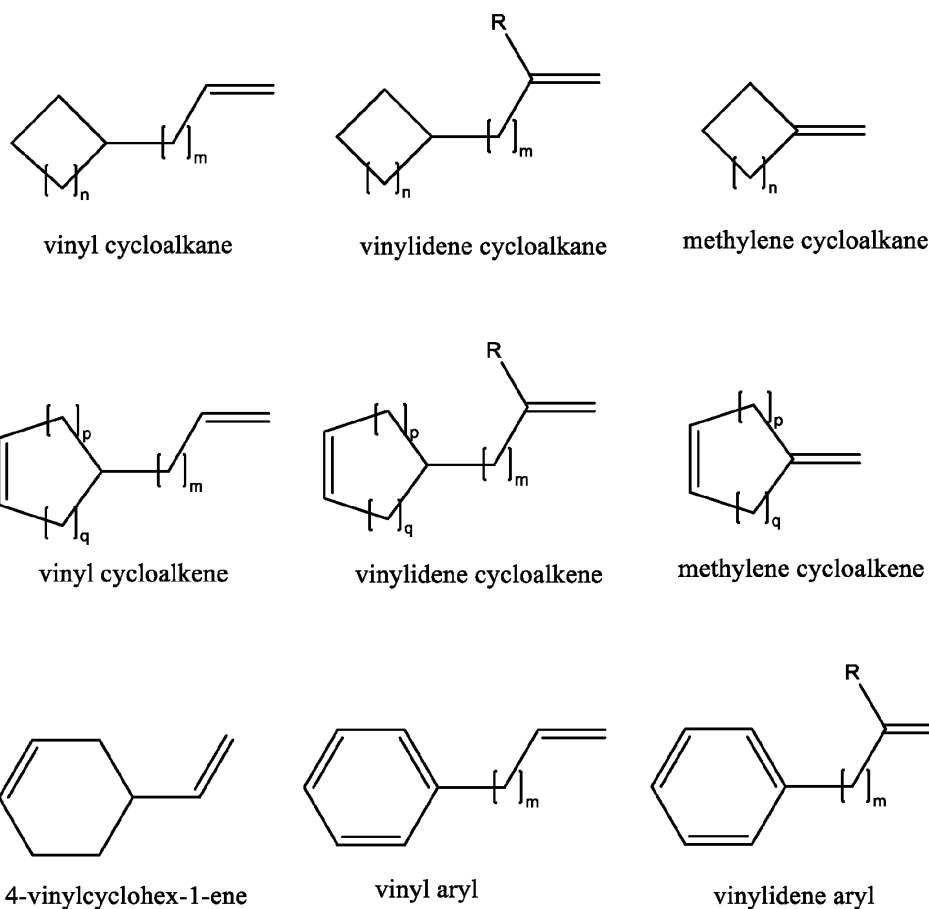
DETAILED DESCRIPTION

- [0014] This disclosure describes the production of cyclic alkanes, wherein one or more alkenes are contacted with a metathesis catalyst to form cyclic alkene dimers, and the hydrogenation of said cyclic alkene dimers yields the cyclic alkanes. The metathesis dimerization process between alkene molecules can be induced by a homogeneous catalyst under mild reaction conditions with a continuous removal of a formed gaseous alkene from the reaction mixture.
- [0015] Provided herein are methods of synthesizing a cyclic alkane, wherein the methods include contacting one or more C₃-C₂₀ alkenes with a metathesis catalyst, wherein the contacting occurs under conditions suitable to yield a cyclic alkene dimer and at least one C₃-C₂₀ alkene is a cyclic alkene; and hydrogenating the cyclic alkene dimer to yield an alkane dimer, wherein the alkane dimer is a cyclic alkane. For example, FIG. 1 depict steps in a non-limiting scheme for synthesizing cyclic alkene dimers and further, synthesizing cyclic alkanes. As used herein, the term “cyclic alkene dimer” refers to a compound resulting from a

carbon-carbon bond forming between two alkene molecules (e.g., a homodimer or heterodimer) wherein at least one C₃-C₂₀ alkene is a cyclic alkene.

[0016] Cyclic alkenes are monomers having an aliphatic or partially unsaturated moiety and a vinyl, methylene or vinylidene containing substituent, or aromatic monomers having a vinyl, or vinylidene containing substituent. Cyclic alkenes include compounds that are monocyclic or bicyclic. Non-limiting examples of cyclic alkenes are illustrated below (shown only as monocyclic monomers, but not limited to monocyclic monomers), wherein m is an integer from 0-20, t and k are integers from 0 to 20 ($2 \leq t+k \leq 20$), y and l are integers from 0 to 4 ($0 \leq y+l \leq 4$), n is an integer from 0-20, p and q are integers from 0 to 18 ($0 < p+q \leq 18$), and w is an integer from 0 to 3; and, R is a C₁₋₁₀ hydrocarbyl substituent. Additionally, the cyclic structure shown below may be saturated, partially unsaturated, or aromatic, and may have one or more additional C₁₋₁₀ hydrocarbyl substituents on the cyclic ring. Likewise, the aromatic cyclic structures shown below may have one or more additional C₁₋₁₀ hydrocarbyl substituents on the cyclic ring. Cyclic alkenes exclude alicyclic olefins having only endocyclic ring unsaturation such as cyclopentene, cyclohexene, cyclooctene and the like. Non-limiting examples of cyclic alkenes include:





[0017] The term “hydrocarbyl substituent” is used herein in accordance with the definition specified by the International Union of Pure and Applied Chemistry (IUPAC): a univalent group formed by removing a hydrogen atom from a hydrocarbon (that is, a group containing only carbon and hydrogen). Non-limiting examples of hydrocarbyl groups include ethyl, phenyl, tolyl, propyl, and the like.

[0018] The method of synthesizing a cyclic alkene dimer can include contacting one or more C₃-C₂₀ alkenes with a metathesis catalyst. The term “C₃-C₂₀ alkene” as used herein, refers to an unsaturated, branched-, straight-chain, or cyclic alkene containing from 3 to 20 carbon atoms, such as, but not limited to, 1-propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, or 1-dodecene, 2-ethyl-1-hexene, 4-methylpent-1-ene, vinylcyclopropane, vinylcyclobutane, vinylcyclopentane, 4-vinylcyclopent-1-ene (also referred to as vinylcyclopentene), vinylcyclohexane, 4-vinylcyclohex-1-ene (also referred to as vinylcyclohexene), vinylcycloheptane,

vinylcyclooctane, vinylcyclononane, vinylcyclodecane, vinylcycloundecane, vinylcyclododecane, 5-vinylnorbornane, 5-vinyl-2-norbornene, allylcyclohexane, and allylcyclooctane, 1,2-di(cyclohex-3-en-1-yl)ethene, and the like. In some embodiments, the linear or branched alkene includes one or more of 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and 4-methylpent-1-ene. In some embodiments, the method includes one C₃-C₂₀ alkene. In some embodiments, the method includes two different C₃-C₂₀ alkenes. In some embodiments, the method includes three or more different C₃-C₂₀ alkenes.

[0019] In some embodiments, the one or more C₃-C₂₀ alkenes are selected from a C₃-C₁₈ linear alkene, a C₅-C₁₄ vinylcycloalkene, a C₆-C₁₀ vinylaryl, and terpenes. The terpene can include any monoterpene or derivative thereof. As used herein, the term “monoterpene” refers to a cyclic compound composed of two isoprene units. In some embodiments, the terpene can include one or more of limonene, pinene, camphene, and sabinene. In some embodiments, the terpene can include limonene or pinene (e.g., β -pinene). The terpenes may be present in any stereoisomeric form or present as a mixture of stereoisomeric forms. For example, if the terpene is pinene, the pinene can be present as α -pinene, β -pinene, or a mixture of α -pinene and β -pinene. In some embodiments, the one or more C₃-C₂₀ alkenes is selected from the group of: C₅-C₁₄ vinylcycloalkenes and C₅-C₁₄ vinylcycloalkanes. For example, the C₅-C₁₄ vinylcycloalkane is vinylcyclopropane, vinylcyclobutane, vinylcyclopentane, or vinylcyclohexane. For example, the C₅-C₁₄ vinylcycloalkene is 4-vinylcyclopent-1-ene, or 4-vinylcyclohex-1-ene. In some embodiments, the one or more C₃-C₂₀ alkenes includes a C₃-C₁₈ linear alkene and a C₅-C₁₄ vinylcycloalkene. In some embodiments, the one or more C₃-C₂₀ alkenes includes a C₃-C₁₈ linear alkene and a C₅-C₁₄ vinylcycloalkane. In some embodiments, the one or more C₃-C₂₀ alkenes includes a C₃-C₁₈ linear alkene, a C₅-C₁₄ vinylcycloalkene, and a C₅-C₁₄ vinylcycloalkane. For example, the one or more C₃-C₂₀ alkenes includes vinylcyclopropane, vinylcyclobutane, vinylcyclopentane, or vinylcyclohexane, vinylcyclohexene, and 1-propene, 1-butene, 2-butene, 1-pentene, 4-methylpent-1-ene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, or 1-dodecene. In some embodiments, the one or more C₃-C₂₀ alkenes includes a terpene and a C₃-C₁₈ linear alkene. For example, the one or more C₃-C₂₀ alkenes includes limonene, pinene, camphene, or sabinene, and 1-propene, 1-butene, 1-pentene, 4-methylpent-1-ene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, or 1-dodecene. In some embodiments, the one or more C₃-C₂₀ alkenes includes a C₆-C₁₀ vinylaryl and a C₃-C₁₈ linear alkene. For example, the one or more C₃-C₂₀ alkenes includes styrene, para-methylstyrene, vinylnaphthylene, allylbenzene, or allyltoluene, and 1-propene, 1-butene, 1-

pentene, 4-methylpent-1-ene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, or 1-dodecene. In some embodiments, the one or more C₃-C₂₀ alkenes are selected from vinylcyclobutane, vinylcyclopentane, vinylcyclopentene, vinylcyclohexane, vinylcyclohexene, styrene, and pinene.

[0020] The metathesis catalyst can be a homogenous catalyst. In some embodiments, the metathesis catalyst includes Ru, Mo, or W. In some embodiments, the metathesis catalyst includes Ru. The metathesis catalyst can include one or more of a Grubbs Catalyst®, a Hoveyda-Grubbs catalyst®, and a Schrock type catalyst. For example, the metathesis catalyst is a first generation Grubbs Catalyst®, a second generation Grubbs Catalyst®, a first generation Hoveyda-Grubbs catalyst®, a second generation Hoveyda-Grubbs catalyst®, or a third generation Grubbs catalyst®. In some embodiments, the metathesis catalyst is [1,3-bis(2,6-diisopropylphenyl)-2-imidazolidinylidene]dichloro[5-(isobutoxycarbonylamido)-2-isopropoxybenzylidene]ruthenium(II), dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](2-isopropoxyphenylmethylene)ruthenium(II), or dichloro[1,3-bis(2,6-isopropylphenyl)-2-imidazolidinylidene]-(benzylidene)(tricyclohexylphosphine)ruthenium(II).

[0021] The metathesis catalyst can be provided in any suitable amount to an ordinary skilled artisan. For example, the metathesis catalyst can be provided in an amount of less than 5 wt%, less than 2 wt%, less than 1 wt%, less than 0.55 wt%, less than 0.1 wt%, less than 0.05 wt%, or less than 0.01 wt%, based on the total weight of the first mixture.

[0022] The methods of the disclosure can include contacting one or more C₃-C₂₀ alkenes with a metathesis catalyst in the presence of a solvent. The solvent can include any suitable aprotic organic solvent, such as, acetone, acetonitrile, pentanes, hexanes, toluene, xylenes, dichloromethane, ethyl acetate, tetrahydrofuran, or the like. In some embodiments, contacting one or more C₃-C₂₀ alkenes with a metathesis catalyst is substantially free of a solvent. As used herein, “substantially solvent free” refers to the contacting one or more C₃-C₂₀ alkenes with a metathesis catalyst includes less than 1 wt% solvent, less than 0.1 wt% solvent, or less than 0.01 wt% solvent.

[0023] The step of contacting one or more C₃-C₂₀ alkenes with a metathesis catalyst can occur at a temperature in a range of about 0°C to about 150°C. For example, the temperature can be in a range of about 10°C to about 150 °C, or about 25°C to about 150°C, or about 50°C to about 100°C, or about 10°C to about 50°C, or about 65°C to about 90°C.

[0024] The step of contacting one or more C₃-C₂₀ alkenes with a metathesis catalyst can occur for 30 seconds to 6 hours or more. For example, contacting the first mixture with a

metathesis catalyst can occur for about 1 minute to about 6 hours, about 30 minutes to about 4 hours, or about 1 hour to about 4 hours.

[0025] The step of contacting of contacting one or more C₃-C₂₀ alkenes with a metathesis catalyst can occur under an inert atmosphere (e.g., N₂ or Ar). In some embodiments, the contacting can occur under an N₂ atmosphere.

[0026] Without intending to be bound by any theory, some of the non-limiting cross-metathesis reactions within the exocyclic C-C double bonds of non-constrained cyclic alkenes are thermodynamically more favorable at elevated temperatures compared to the ring opening metathesis polymerization involving the endocyclic C-C double bonds.

[0027] The cyclic alkene dimer can include a homodimer, a heterodimer, or a mixture of heterodimers and homodimers. As used herein, the term "homodimer" (e.g., cyclic alkene homodimer) refers to a compound resulting from a carbon-carbon bond forming between two of the same alkene molecules. As used herein, the term "heterodimer" (e.g., cyclic alkene heterodimer) refers to a compound resulting from a carbon-carbon bond forming between two different alkene molecules.

[0028] The contacting one or more C₃-C₂₀ alkenes with a metathesis catalyst can yield a cyclic alkene dimer and ethylene.

[0029] The methods of the disclosure further include hydrogenating the cyclic alkene dimer to yield an alkane dimer, wherein the alkane dimer is a cyclic alkane. The step of hydrogenating can include contacting the cyclic alkene dimer with a hydrogenation catalyst and H₂. In some embodiments, the hydrogenation catalyst can include a metal, a metal oxide, or both. The hydrogenation catalyst can be one or more of NiO, Ni, Pd/C, Ru, Ru/C, Ru₂O₃, Ru/alumina, PdO, Pd, Pt, Ir, PtO₂, dichlorotris(triphenylphosphine)ruthenium(II), or cyclooctadiene rhodium(I) chloride. In some embodiments, the hydrogenation catalyst is Pd/C. In some embodiments, the hydrogenation catalyst includes Ru/alumina.

[0030] The hydrogenation catalyst can be provided in any suitable amount to an ordinary skilled artisan. For example, the hydrogenation catalyst can be provided in an amount of less than 10 mol%, less than 5 mol%, less than 2 mol%, less than 1 mol%, less than 0.5 mol%, less than 0.1 mol%, or less than 0.05 mol%, based on the amount of mols of the cyclic alkene dimer.

[0031] The step of hydrogenating can include H₂ as a gas, and the H₂ can be provided at a pressure of at least 5 psi. For example, the H₂ can be provided at a pressure of about 10 psi to about 2000 psi, or about 25 psi to about 100 psi, or about 100 psi to about 1500 psi, or about

250 psi to about 750 psi. In some embodiments, the H₂ can be provided at a pressure of about 20 psi to about 1250 psi, or about 20 psi to about 200 psi, or about 750 psi to about 1100 psi.

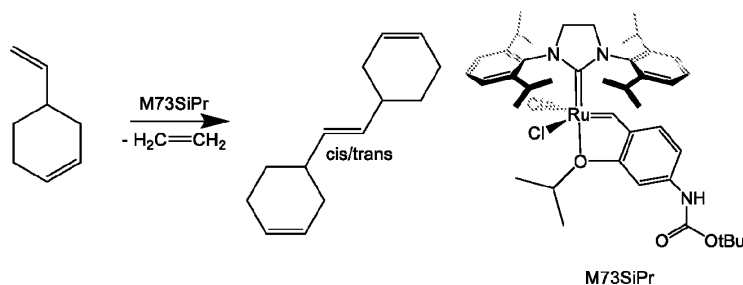
[0032] The hydrogenating can occur at a temperature of less than about 200°C. For example, the hydrogenating can occur at a temperature in a range of about 50°C to about 175°C, or about 75°C to about 150°C, or about 90°C to about 130°C.

[0033] The step of hydrogenating can occur for about 10 minutes to about 1 day. For example, the step of hydrogenating can occur for about 30 minutes to about 15 hours, or about 1 hour to about 6 hours, or about 6 hours to about 15 hours, or about 1 hour to about 4 hours.

[0034] The step of hydrogenating yields an alkane dimer, wherein the alkane dimer is a cyclic alkane. In some embodiments, the cyclic alkane is 1,2-dicyclohexylethane, 1,2-dicyclopentylethane, 1,2-dicyclobutylethane, or (1S,5S)-6,6-dimethyl-2-octylbicyclo[3.1.1]heptane.

EXAMPLES

Example 1. Preparation of 1,2-di(cyclohex-3-en-1-yl)ethene



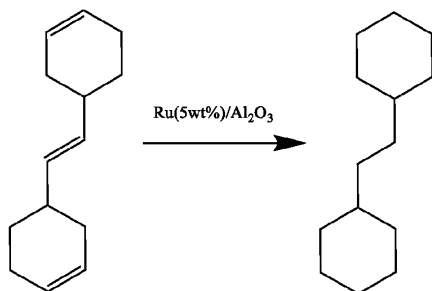
[0035] Solid catalyst [1,3-bis(2,6-diisopropylphenyl)-2-imidazolidinylidene]dichloro[5-(isobutoxycarbonylamido)-2-isopropoxybenzylidene]ruthenium(II) (200 mg, 0.242 mmol) was added to an open flask containing 4-vinylcyclohexene (2.0 L, 1.66 kg, 15.3 mol) at 45°C under magnetic stirring resulting in ethylene gas formation. After no ethylene formation was observed (typically in about 1 hour), a new portion of the catalyst was added (200 mg). This step was repeated several times until no gas evolution was observed. In total, 1.0 g (1.21 mmol) of the catalyst was added over about 4 h. The reaction mixture was then filtered through a silica plug to give 1.6 L of a colorless liquid containing around 80% yield of the cyclic alkene dimer, according to the GC analysis shown below in Table 1 and FIG. 2. The pure cyclic alkene dimer was isolated by removing unreacted 4-vinylcyclohexene by heating the mixture to 130°C at ambient pressure and subsequently distilling the residue at 130°C and

0.5 Torr. ^1H NMR (400 MHz, C_6D_6): δ 5.67 (m, 4H), 5.40 (m, 2H), 2.22-2.15 (m, 2H), 2.09-2.03 (m, 2H), 2.00-1.96 (m, 4H), 1.87-1.80 (m, 2H), 1.71-1.67 (m, 2H), 1.40-1.32 (m, 2H).

Table 1. GC composition of the reaction mixture.

Identity	Retention Time (min)	Area (a.u.)	Peak Area (%)
4-vinylcyclohexene	3.023	13112308	20.2
Nonane	3.705	5569213	
Cyclic alkene dimer (<i>cis</i>)	8.506	7855293	12.1
Cyclic alkene dimer (<i>trans</i>)	8.735	42676178	65.8
Other		1198283	1.8

Example 2. Preparation of 1,2-dicyclohexylethane

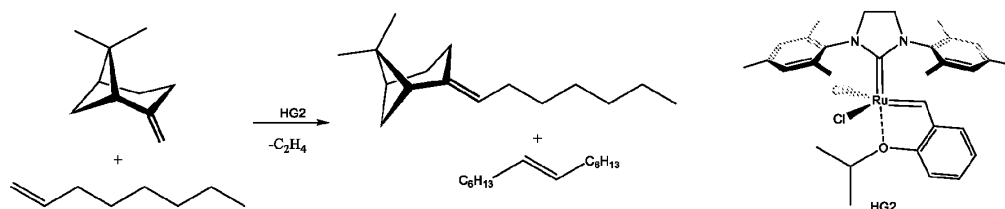


[0036] 1,2-di(cyclohex-3-en-1-yl)ethane (cyclic alkene dimer) obtained in Example 1 (50 mL) was hydrogenated in a 500 mL Parr reactor using 100 mg of Ru/ Al_2O_3 (5 wt% Ru) catalyst and 1000 psi H_2 at 100°C over 2 hours. The reaction mixture was filtered through a celite plug to give a colorless liquid in a qualitative yield, according to GC analysis (Table 2 and FIG. 3). ^1H NMR spectrum for the product showed minimal unsaturation (<0.5 %), according to the absence of the product resonance signals in the range from 10 to 5 ppm. ^1H NMR (400 MHz, C_6D_6): δ 1.73-1.63 (m, 9H), 1.29-1.10 (m, 12H), 0.92-0.82 (m, 5H).

Table 2. GC Composition for the reaction mixture.

Identity	Retention Time (min)	Area (a.u.)	Peak Area (%)
Nonane	3.705	4623052	
hydrogenated dimer	8.62	76829694	99.2
Other		655561	0.8

Example 3. Metathetical heterodimerization of terpene and 1-octene

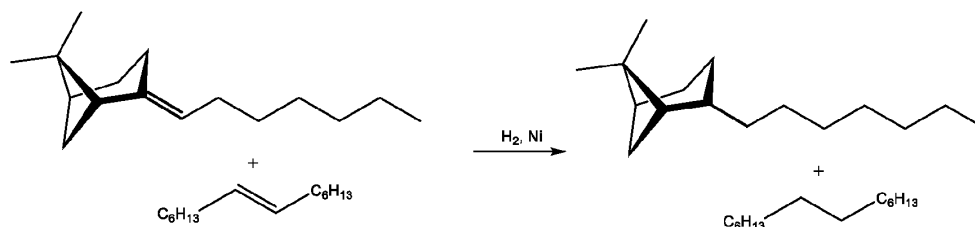


[0037] 1-Octene and beta-pinene were dried over AZ300 (UOP Adsorbent AZ-300, A Honeywell Company), purged with nitrogen and stored above activated molecular sieves (4 Å) for 12 hours. Solid dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](2-isopropoxyphenylmethylene)ruthenium(II) (0.3 g, 0.479 mmol) was added to a mixture of 1-octene (300 g, 2.14 mol, 1 equivalent) and beta-pinene (351 g, 2.58 mol, 1.2 equivalents) at 75°C in a 1L open flask. The mixture was stirred for 3 hours under the intense N₂ sparge. The filtration through an alumina plug gave a viscous liquid, which was distilled under reduced pressure with the collection of the following fractions: 1st fraction - 164 g, 5 Torr, boiling point (bp) < 80°C; 2nd fraction - 94 g, 3-5 Torr, bp 80-110°C; and 3rd fraction - 34 g, < 1 Torr, 110°C. Residue included about 50 g of a viscous yellow liquid. GC analysis for the reaction mixture and distilled fractions shows substantial isomerization of the beta-pinene fragment into various terpenes (Table 3 and FIG. 4).

Table 3. GC Composition for the fractions obtained in Example 3

	Composition, wt%			Total, g
	1 st fraction	2 nd fraction	3 rd fraction	
pinene-octene (dimer)	1.0	41.1	70.7	64.3
all dimers	9.0	89.9	96.5	132.0

Example 4. Hydrogenation of pinene-octene dimers

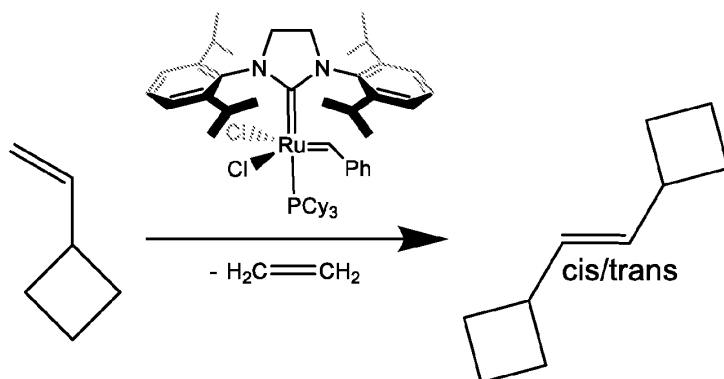


[0038] The solution of the 3rd distillation fraction (Example 3, 23.5 g) in *n*-hexane (50 mL) was hydrogenated in a 500 mL Parr reactor using 0.47 g of commercial NiSat® hydrogenation catalyst (2 wt%) and 650 psi H₂. The reactor was heated to 230°C and agitated at 400 rpm over 2 hours. The reactor was then cooled to ambient temperature, depressurized, and opened. The obtained reaction mixture was filtered through a celite plug to give a colorless liquid. Hexane was removed under reduced pressure to give 18.5 g of the product. ¹H NMR spectrum for the product showed no unsaturation according to the absence of the product resonance signals in the range from 10 ppm to 3 ppm. GC-MS analysis shows ca 57 wt% of hydrogenated octene-pinene dimers in the product (Table 4 and FIG. 5).

Table 4. GC-MS composition for the hydrogenated product obtained in Example 4

Identity	Retention Time, min	Area, a.u.	Peak Area, %
nonane	3.70	4665304	-
Hydrogenated octene-octene dimer	7.86	15302645	20.35
Hydrogenated octene-nonene dimer	8.50	787159	1.05
Hydrogenated octene-pinene dimers	8.79-9.37	42721188	56.80
Others (oligomers)	10.02-12.89	16401353	21.81

Example 5. Preparation of 1,2-Dicyclobutylethene



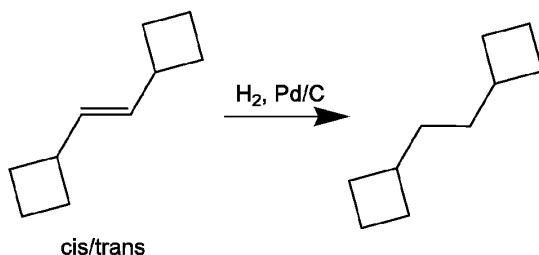
[0039] Dichloro[1,3-bis(2,6-isopropylphenyl)-2-imidazolidinylidene]-(benzylidene)(tricyclohexylphosphine)ruthenium(II) (1.0 mg, 0.00153 mmol) was added to neat vinylcyclobutane (5.0 g, 60.9 mmol) in a 20 mL vial at ambient temperature. Gas evolution was observed. The mixture was stirred in an open vial for 3 hours. Then, the reaction temperature was elevated to 35°C, and the mixture was stirred for additional 1 hour. The reaction mixture was filtered through an alumina plug to give 0.93 g of the product

containing 93.5 wt% of 1,2-dicyclobutylethenes ($E/Z = 6.7$), as shown by GC analysis (Table 5 and FIG. 6). ^1H NMR (400 MHz, C_6D_6): δ 5.49 (m, 1.80H, *trans*), 5.39 (m, 0.2H, *cis*), 3.14-3.08 (m, 0.2H, *cis*), 2.89-2.73 (m, 1.8H, *trans*), 2.07-1.99 (m, 4H), 1.86-1.65 (m, 8H). ^{13}C NMR (101 MHz, C_6D_6) for *cis* isomer: δ 133.77, 34.16, 29.96, 18.95; and for *trans* isomer: δ 132.84, 38.40, 28.90, 18.52.

Table 5. Composition of the reaction mixture by GC-MS

Identity	Retention Time, min	Area, a.u.	Peak Area, %
nonane	3.70	5364488	-
dimer <i>cis</i> -isomer	5.35	5230251	12.17
dimer <i>trans</i> -isomer	5.50	34949183	81.35
others	7.19-7.84	2781756	6.48

Example 6. Preparation of 1,2-Dicyclobutylethane



[0040] 1,2-Dicyclobutylethene (1.50 g, 11.0 mmol, mixture of E/Z isomers) was hydrogenated in the presence of Pd/C (10 wt%, 50 mg) at 120°C and 40 psi H_2 over 12 hours. The Pd/C catalyst was then removed by filtration. The resulting liquid contained 89 wt% of the targeted product, according to the GC-MS analysis (Table 6 and FIG. 7). ^1H NMR (400 MHz, C_6D_6): δ 2.15 (m, 2H), 2.01 (m, 4H), 1.80 (m, 4H), 1.55 (m, 4H), 1.24 (m, 4H). ^{13}C NMR (101 MHz, C_6D_6): δ 36.13, 34.55, 28.38, 18.48.

Table 6. GC composition of the reaction mixture obtained in Example 6

Identity	Retention Time, min	Area, a.u.	Peak Area, %
ethylcyclobutane	1.485	414002.4	1.14
nonane	3.694	4759010	-
1,2-dicyclobutylethane	5.287	32172211	88.61
others		3719860	10.25

[0041] Various embodiments of the features of this disclosure are described herein. However, it should be understood that such embodiments are provided merely by way of example, and numerous variations, changes, and substitutions can occur to those skilled in the art without departing from the scope of this disclosure. It should also be understood that various alternatives to the specific embodiments described herein are also within the scope of this disclosure.

[0042] Embodiment 1 is a method of synthesizing a cyclic alkane, the method comprising:

contacting one or more C₃-C₂₀ alkenes with a metathesis catalyst, wherein the contacting occurs under conditions suitable to yield a cyclic alkene dimer and wherein at least one C₃-C₂₀ alkene is a cyclic alkene; and

hydrogenating the cyclic alkene dimer to yield an alkane dimer, wherein the alkane dimer is a cyclic alkane.

[0043] Embodiment 2 is the method of embodiment 1, wherein at least one of the one or more C₃-C₂₀ alkenes comprises a C₃-C₁₈ linear alkene, a C₅-C₁₄ vinylcycloalkane, a C₅-C₁₄ vinylcycloalkene, a C₆-C₁₀ vinylaryl, or a terpene.

[0044] Embodiment 3 is the method of embodiment 1 or 2, wherein at least one of the one or more C₃-C₂₀ alkenes comprises vinylcyclobutane, vinylcyclopentane, vinylcyclopentene, vinylcyclohexane, vinylcyclohexene, styrene, para-methylstyrene, or pinene.

[0045] Embodiment 4 is the method of any one of embodiments 1-3, wherein the metathesis catalyst is a homogenous catalyst.

[0046] Embodiment 5 is the method of any one of embodiments 1-4, wherein the metathesis catalyst comprises Ru, Mo, or W.

[0047] Embodiment 6 is the method of any one of embodiments 1-5, wherein the metathesis catalyst comprises one or more of a Grubbs Catalyst®, a Hoveyda-Grubbs catalyst®, and a Schrock type catalyst.

[0048] Embodiment 7 is the method of embodiment 6, wherein the metathesis catalyst comprises a first generation Grubbs Catalyst®, a second generation Grubbs Catalyst®, a first generation Hoveyda-Grubbs catalyst®, a second generation Hoveyda-Grubbs catalyst®, or a third generation Grubbs catalyst®.

[0049] Embodiment 8 is the method of any one of embodiments 1-7, wherein the contacting occurs substantially solvent free.

[0050] Embodiment 9 is the method of any one of embodiments 1-8, wherein the contacting occurs at a temperature in a range of about 0°C to about 150°C.

[0051] Embodiment 10 is the method of any one of embodiments 1-9, wherein the cyclic alkene dimer comprises a homodimer, a heterodimer, or a mixture of heterodimers and homodimers.

[0052] Embodiment 11 is the method of any one of embodiments 1-10, wherein the hydrogenating comprises contacting the cyclic alkene dimer with a hydrogenation catalyst and H₂.

[0053] Embodiment 12 is the method of embodiment 11, wherein the hydrogenation catalyst comprises a metal, a metal oxide, or both.

[0054] Embodiment 13 is the method of embodiment 11 or 12, wherein the hydrogenation catalyst comprises NiO, Ni, Pd/C, Ru, Ru/C, Ru₂O₃, Ru/alumina, PdO, Pd, Pt, Ir, or PtO₂.

[0055] Embodiment 14 is the method of any one of embodiments 1-13, wherein the hydrogenating occurs at a temperature of less than about 200°C, or in a range of about 50°C to about 175°C, or about 75°C to about 150°C.

[0056] Embodiment 15 is the method of any one of embodiments 11-14, wherein the hydrogenating comprises H₂ at a pressure of about 20 psi to about 1250 psi, or about 20 psi to about 200 psi, or about 750 psi to about 1100 psi.

[0057] Although this disclosure contains many specific embodiment details, these should not be construed as limitations on the scope of the subject matter or on the scope of what may be claimed, but rather as descriptions of features that may be specific to particular embodiments. Certain features that are described in this disclosure in the context of separate embodiments can also be implemented, in combination, in a single embodiment. Conversely, various features that are described in the context of a single embodiment can also be implemented in multiple embodiments, separately, or in any suitable sub-combination. Moreover, although previously described features may be described as acting in certain combinations and even initially claimed as such, one or more features from a claimed combination can, in some cases, be excised from the combination, and the claimed combination may be directed to a sub-combination or variation of a sub-combination.

[0058] Particular embodiments of the subject matter have been described. Other embodiments, alterations, and permutations of the described embodiments are within the scope of the following claims as will be apparent to those skilled in the art. While operations are depicted in the drawings or claims in a particular order, this should not be understood as

requiring that such operations be performed in the particular order shown or in sequential order, or that all illustrated operations be performed (some operations may be considered optional), to achieve desirable results.

[0059] Accordingly, the previously described example embodiments do not define or constrain this disclosure. Other changes, substitutions, and alterations are also possible without departing from the spirit and scope of this disclosure.

WHAT IS CLAIMED IS:

1. A method of synthesizing a cyclic alkane, the method comprising:
contacting one or more C₃-C₂₀ alkenes with a metathesis catalyst, wherein the contacting occurs under conditions suitable to yield a cyclic alkene dimer and wherein at least one C₃-C₂₀ alkene is a cyclic alkene; and
hydrogenating the cyclic alkene dimer to yield an alkane dimer, wherein the alkane dimer is a cyclic alkane.
2. The method of claim 1, wherein at least one of the one or more C₃-C₂₀ alkenes comprises a C₃-C₁₈ linear alkene, a C₅-C₁₄ vinylcycloalkane, a C₅-C₁₄ vinylcycloalkene, a C₆-C₁₀ vinylaryl, or a terpene.
3. The method of claim 1 or 2, wherein at least one of the one or more C₃-C₂₀ alkenes comprises vinylcyclobutane, vinylcyclopentane, vinylcyclopentene, vinylcyclohexane, vinylcyclohexene, styrene, para-methylstyrene, or pinene.
4. The method of any one of claims 1-3, wherein the metathesis catalyst is a homogenous catalyst.
5. The method of any one of claims 1-4, wherein the metathesis catalyst comprises Ru, Mo, or W.
6. The method of any one of claims 1-5, wherein the metathesis catalyst comprises one or more of a Grubbs Catalyst®, a Hoveyda-Grubbs catalyst®, and a Schrock type catalyst.
7. The method of claim 6, wherein the metathesis catalyst comprises a first generation Grubbs Catalyst®, a second generation Grubbs Catalyst®, a first generation Hoveyda-Grubbs catalyst®, a second generation Hoveyda-Grubbs catalyst®, or a third generation Grubbs catalyst®.
8. The method of any one of claims 1-7, wherein the contacting occurs substantially solvent free.
9. The method of any one of claims 1-8, wherein the contacting occurs at a temperature in a range of about 0°C to about 150°C.
10. The method of any one of claims 1-9, wherein the cyclic alkene dimer comprises a homodimer, a heterodimer, or a mixture of heterodimers and homodimers.
11. The method of any one of claims 1-10, wherein the hydrogenating comprises contacting the cyclic alkene dimer with a hydrogenation catalyst and H₂.
12. The method of claim 11, wherein the hydrogenation catalyst comprises a metal, a metal oxide, or both.

13. The method of claim 11 or 12, wherein the hydrogenation catalyst comprises NiO, Ni, Pd/C, Ru, Ru/C, Ru₂O₃, Ru/alumina, PdO, Pd, Pt, Ir, or PtO₂.
14. The method of any one of claims 1-13, wherein the hydrogenating occurs at a temperature of less than about 200°C, or in a range of about 50°C to about 175°C, or about 75°C to about 150°C.
15. The method of any one of claims 11-14, wherein the hydrogenating comprises H₂ at a pressure of about 20 psi to about 1250 psi, or about 20 psi to about 200 psi, or about 750 psi to about 1100 psi.