Iron(III) Catalyzed Dimerization of Cycloolefins: Synthesis of High-Density Fuel Candidates

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1. General Remarks

All manipulations were carried out under Argon atmosphere using Schlenk or vacuum line techniques. Pentane was dried under argon over sodium metal and distilled prior to use. Anhydrous cyclopentene, cyclohexene, cyclohexene, 1-methylcyclohexene, 3-methylcyclohexene, methyl 3-cyclohexene-1-carboxylate and phenylcyclohexene were purchased either from Aldrich or TCI laboratories and used as received. The anhydrous metal complexes FeF₃, FeCl₃, FeBr₃, Fe(Acac)₃ were purchased from Aldrich and TCI laboratories and used as received. Anhydrous 10 % Pd/C and 5% Pt on Alumina were purchased from Aldrich and used without further purification. NMR spectra were recorded on a 400 MHz Jeol spectrometer in CDCl₃. GC-MS were recorded on Thermo Fisher Scientific spectrometer with fused silica capillary column (30m length x 0.25 mm ID x 0.25 um film thickness), using the following GC method:

Detector : FID:

Starting temperature: 40°C; Time at starting temp: 2 min

Ramp1: 10° C/min up to 250° C with hold time = 2 to 10 min.

Flow rate(carrier): 1.2 ml/min(He); Split ratio: 83

Inlet temperature: 250°C; Detector temperature: 250°C.

All flash column chromatography was performed on small columns (5 x 60 mm) of Silica Gel (Aldrich), 700-230 mesh, 60 Å, pore volume $0.75 \text{ cm}^3/\text{g}$. The fractional distillation was performed after all the metal complex was removed from the crude mixture in a Buchi glass Oven B-585 under reduced pressure.

2. Experimental Procedures

2.1 Dimerization of cyclohexene (5): Using the general method, we could isolate the corresponding cyclohexyl-cyclohexene dimer mixture in almost 99% purity. The major regioisomer is present as 95% of the product mixture (by GC-MS analysis) and was identified as 1-cyclohexylcyclohexene (I, 12 in manuscript), with the other regioisomers appearing as minor components which correspond to 3-cyclohexylcyclohexene (II, 11 in manuscript) and 4-cyclohexylcyclohexene (III). The identity of isomers was ascertained by synthesis of authentic samples of isomers I-III, using known literature protocols^{S1-S3} and comparison with experimentally obtained dimer mixtures.



2.1.1.1 Catalytic transformation of di-substituted cycloalkene to a more substituted cycloalkene:

In a typical reaction 0.91 mmol of cycloxene dimer **II** (**11** in manuscript) was charged to a Kontes Airless 25ml storage vessel tube, and 10 mol % of FeCl₃ (0.015g) was added to this mixture. The mixture was degassed using the freeze-pump-thaw technique. Immediately the mixture was heated to 120 C in an oil bath. The reaction was monitored by ¹³C NMR Spectroscopy and GC-MS analysis. After 2 days of heating, the reaction was stopped and the mixture was initially filtered through celite in the presence of pentane. Further purification was carried out using a silica gel column and eluted with pentanes to completely remove any remaining traces of the metal complex. The volatiles were removed to leave a mixture of the dimer products corresponding to the cyclohexene dimer of the type **I** (**12** in manuscript), in almost 80%.

2.1.2 Dimerization of cyclooctene (1): Using the general method, we could isolate the corresponding

cyclooctylcyclooctene product mixture in almost 99% purity. 2 different isomeric species were observed by GC-MS analysis, the major isomer being identified as 1-cyclooctylcyclooctene (**IV**, **2a** in manuscript), and the 1,1-bicyclooctylidene (**V**, **2b** in manuscript). ¹³C and ¹H NMR spectra are in agreement with those reported in the literature (see below).^{S4}



2.1.3 Dimerization of 1-methylcyclohexene (8): Using the general method, we could isolate the corresponding mixture of dimers (MW: 192). Two major isomers observed by GC-MS analysis, the major isomer being identified as the 1-methyl-3-(2-methylcyclohexyl)cyclohexene (VI), and the 3-methyl-1-(2-methylcyclohexyl)cyclohexene (VII). We have been unable to separate this isomeric mixture, but we could identify the isomers by ¹³C and ¹H NMR spectroscopy.



Curiously, FeBr₃ presents higher selectivity in the dimerization of 1-methylcyclohexene, giving predominantly 3-methyl-1-(2-methylcyclohexyl)cyclohexene (**VII**) perhaps suggesting a more effective isomerization reaction occurs with this metal salt.

2.1.4 Dimerization of 1-phenylcyclohexene (14): Using the general method, we could determine the major product of the dimerization of 1-phenylcyclohexene, which was the hydrogenated phenylcyclohexane

(VIII), MW: 160 g/mol and only traces of the desired product (IX, the position of the isolated double bond could not be determined) MW: 316 g/mol, were observed. Additionally a dimer corresponding to a dehydrogenated product (X) with molecular weight of 312 g/mol was also observed.



Both the hydrogenated product (VIII) and the dehydrogenated dimer (X) could be isolated by distillation under reduced pressure.

2.2 General Method: Metal catalyzed hydrogenation of the dimer mixture



In order to identify the mixture of isomers we chose to hydrogenate them to obtain a single compound. In a typical experiment, the mixture of dimers was added as a pentane solution schlenk flask and 3-10 mol% of the Pd/C complex was added. This mixture was degassed using the freeze-pump-thaw technique, and then it was saturated with hydrogen atmosphere using a needle directly from the hydrogen source and then a balloon was filled with hydrogen and connected to the reaction flask immediately. The reaction was then stirred for a period between 1 to 4d. After that time, the solution was filtered over silica gel, washed several times and the volatiles were removed under reduced pressure to generate the reduced product. At this stage we were able to isolate the reduced products: bis(cyclohexane) (XI), 2,3'-dimethyl-bis(cyclohexane) (XII) and bis(cyclooctane) (XIII, 3 in manuscript). In the presence of Pt/Alumina, the reaction requires longer reactions times, elevated

temperatures and the absence of solvent.

2.3 Testing the effects of acid on catalytic dimerization:



In a typical experiment, cycloalkene is added to a Schlenk flask and exposed to (excess) concentrated HCl. The reaction mixture was then stirred at room temperature from 1 to 4 days under an inert atmosphere. Monitoring of the reaction was performed using GC-MS analysis. After workup of the mixture, the solution was eluted with pentanes through a small column of silica gel. No dimer product was formed.

2.4 Testing chlorocycloalkanes as potential intermediates in the catalytic dimerization of cycloalkenes:



In a typical reaction 1 mmol of cycloalkene was charged to a Kontes Airless 25ml storage vessel tube, and 2 mmol of (commercially available) chlorocyclohexane was added to this mixture. The mixture was degassed using the freeze-pump-thaw technique and kept under argon atmosphere. Immediately the mixture was heated to 120°C in an oil bath. The reaction was monitored by GC-MS analysis. After 4 days of heating, the reaction was stopped. No dimer mixture associated with the cycloalkene-cyclohexane mixture was observed. In the presence of 10 mol% FeCl₃, the reaction does not generate the expected cycloalkene-cyclohexane dimer, but only traces of the dimer mixture associated with the cycloolefin substrate alone.

3. GC_MS Characterization Data



3.1 Dimerization of cyclopentene

Figure S1: GC-MS showing a typical spectrum of the catalytic dimerization of cyclopentene into cyclopentene-cyclopentane dimer mixture (XV).



Figure S2: GC-MS showing fragmentation of the cyclopentene dimer mixture

3.2 Dimerization of cyclohexene



Figure S3: GC-MS showing fragmentation of the cyclohexene dimer mixture.

3.2.1 Detection of a chloroderivative in the dimerization of cyclohexene



Figure S4: GC-MS showing a typical spectrum for the non optimized dimerization of cyclohexene



3.2.2 Identification of the isomers from dimerization of cyclohexene

Figure S5: GC-MS Showing the identification of isomers associated with the dimerization of cyclohexene

3.2.3 Catalytic transformation of di-substituted cycloalkene to a more substituted cycloalkene



Figure S6: ¹³C NMR Spectroscopy showing the thermal transformation of disubstituted dimer(I) into the trisubstituted dimer(II).

3.3 Dimerization of cycloheptene



Figure S7: GC-MS showing a typical spectrum for the catalytic dimerization of cycloheptene into cycloheptene-cycloheptane dimer mixture (XVI).



Figure S8: GC-MS showing the fragmentation of cycloheptene-cycloheptane dimer mixture.

3.4 Dimerization of cyclooctene



Figure S9: GC-MS showing a typical spectrum for the catalytic dimerization of cyclooctene into cyclooctene-cyclooctane dimer mixture (V and IV).



Figure S10: GC-MS showing the fragmentation of cyclooctene dimer mixture.



Figure S11: GC-MS showing the fragmentation of chlorocyclooctane

3.5 Dimerization of 1-methylcyclohexene



Figure S12: GC-MS showing a typical spectrum for the catalytic dimerization of 1-methylcyclohexene into 1-methylcyclohexene-1-methylcyclohexane dimer mixture (*).



Figure S13: GC-MS showing a typical spectrum for the catalytic dimerization of 1-methylcyclohexene into 1-methylcyclohexenemethyl-cyclohexane dimer mixture.



Figure S14: GC-MS showing the fragmentation of 1-methylcyhexene-methylcyclohexane dimer.



Figure S15: GC-MS showing a typical spectrum of the isomers associated with the dehydrogenated trimer (XVIII) observed in the dimerization of 1-methylcyclohexene.

3.6 Dimerization of 3-methylcyclohexene



Figure S16: GC-MS showing the fragmentation of 3-methyl-6-(2-methylcyclohexyl)cyclohexene dimer mixture.



Figure S17: GC-MS showing the fragmentation of 3-methyl-6-(2-methylcyclohexyl)cyclohexene

3.7 Dimerization of 3-cyclohexene-1-carboxylate



Figure S18: GC-MS showing the fragmentation of 3-cyclohexene-1-carboxylate dimer.

3.8 Dimerization of alpha-pinene



Figure S19: GC-MS showing the fragmentation of alpha-pinene dimer mixture

3.9 Dimerization of phenylcyclohexene



Figure S20: GC-MS showing a typical spectrum of the catalytic dimerization of 1-phenylcyclohexene (Δ) into the unexpected hydrogenated phenylcyclohexane (Δ).



Figure S21: GC-MS showing the fragmentation of phenycyclohexane (VIII)



Figure S22: GC-MS showing the fragmentation of phenylcyclohexene dimer (IX)



Figure S23: GC-MS showing the fragmentation of isolated dehydrogenated phenyclcyclohexene dimer (X)

3.10 Pd/C reduction of cyclohexene dimers



Figure S24. Pd/C catalyzed hydrogenation of cyclohexyl-cyclohexene reaction mixture containing isomers(I,II and III) into bis(cyclohexyl) (XI).



Figure S25: GC-MS showing the fragmentation of isolated bi(cyclohexane)



Figure S26: GC-MS showing the Pd/C catalyzed Hydrogenation of a dimeric mixture containing (VII and VI) into 2,3'-dimethylbis(cyclohexane) (XII).^a Note: The dimeric mixture was obtained from the reaction of Febr₃ with 1 methylcyclohexene.

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Figure S27: GC-MS showing the fragmentation of the 2,3'-dimethylbis(cyclohexane) (XII).

Figure S28: GC-MS showing the fragmentation of proposed dehydrogenative product (XIV), obtained from the hydrogenation of 1methylcyclohexene dimmers (VI and VII). In the presence of Pt/Alumina at 230°C.

3.12 Pd/C reduction of cyclooctene dimers

Figure S29: GC-MS showing the Pd/C catalyzed Hydrogenation of cyclooctyl-cyclooctene (1) into the corresponding bis(cyclooctane) (*).

Figure S30: GC-MS showing the fragmentation of isolated bi(cyclooctyl)

Figure S31: GC-MS fragmentation comparison between the isolated bis(cyclooctyl) (XIII) and a commercially available sample.

3.13 PtO2 reduction of alpha-pinene dimers

Figure S32: GC-MS showing the PtO2 catalyzed Hydrogenation of alpha-pinene dimers into the corresponding saturated systems.

3.14 Testing the acid catalyzed effect of cycloalkenes with HCl:

Figure S33: GC-MS showing the non dimerization of 1-methylcyclohexene in the presence of HCl.

Additionally we explore the same reaction but in the presence of the FeCl₃ complex (Figure S34).

Figure S34: GC-MS showing the effect of the HCl in the dimerization of 1-methylcyclohexene in the presence of FeCl₃.

Figure S35: GC-MS showing the presence of chlorocycloalkane to be the result of a non-product side reaction.

Figure S36: GC-MS showing the no effect of the chlorocyclohexane in the catalytic dimerization of cyclooctene

3.16 Probing the effects of added water on dimerization of 1-methylcyclohexene

Figure S37. GC-MS comparing dimerization of 1-methylcyclohexene under anhydrous (top) and wet (10 mol %, 1:1 water:catalyst) conditions

4. Auxiliary Tables:

 Table S1: Catalytic transformation of di-substituted cycloalkene to a more substituted cycloalkene

Reaction conditions: cycloalkene dimer mixture; 10 mol% FeCl₃ Temperature 120°C. Argon atmosphere.

Table S2: Pd/C or Pt/Alumina catalyzed hydrogenation of dimer mixtures of cyclohexene(1,2), cyclooctene(3) and 1-methylcyclohexene(4,5 and 6)

Entry	Catalyst	Temperature	Solvent	Dimer	Hydro- genated	Yield
		(°C)		Mol. Weight	Product	(%) ^{a/b}
1	Pd/C	RT	Pentanes	164	166	100/(100)
2	Pt/Alumina	230	Neat	164	166	100/(66)
3	Pd/C	RT	Pentanes	220	222	100/(100)
4	Pd/C	RT	Pentanes	192	194	No reaction
5	Pd/C	RT	Pentanes	192	194	$100/(50)^{c}$
6	Pt/Alumina	230	Neat	192	194	$100/(18)^{d}$
7	Pd/C	RT	Pentanes	222	220	$100(90)^{e}$

All the reactions were performed for a period of 1 day. ^a % consumption of the substrate calculated by GC_MAS. ^b: Selectivity of the desired reduced product calculated by GC-MS. ^c The reaction took 4 days to reach completion. ^d Only 18% of the reduced product was observed, rest is a mixture of different species containing mainly the dehydrogenated product with a molecular weight of 188. ^e Dimer mixture from FeBr₃ catalyzed reaction. Hydrogenation time 2 days.

Table S3: Chlorocycloalkane as potential intermediate in the catalytic dimerization of cycloalkenes

Entry	Substrate	Time (Day)	Temp (°C)	Substrate Consumption (%)	Chlorocyclohexane Consumption (%)	Mixed Isomer Cyclohexane-cycloalkene (%)
1	1-methylcyclohexene	1	RT	0	0	0
2	1-methylcyclohexene + FeCl ₃	1	RT	15	0	0
3	Cyclooctene	1	120	0	0	0
4	$Cyclooctene + FeCl_3$	4	120	10	0	0

Table S4: Preliminary Data Screening of commercially available copper salts for activity in COE dimerization^a

	Entry			
		Catalyst	Time	Cyclooctene Consumption
		(10mol%)	(hr)	(%) ^b
	1	CuO	20	No reaction
	2	Cu ₂ O	20	No reaction
	3	CuCl	20	No reaction
_	4	CuCl ₂	20	No reaction

a) Reactions conditions: Neat COE, 110°C, Specified time. b) As determined by GC-MS analysis

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Entry	Catalyst (10mol%)	Time (hr)	Substrate Consumption (%)	Dimer Yield (%) ^b	Chloro-cycloalkane Yield (%) ^b
1	FeF ₃	24	0	0	0
2	FeCl ₃	24	99	73	5
3	FeBr ₃	24	96	75	16
4	Fe(Acac)	24	0	0	0

a) Reactions conditions: Neat 1-methylcyclohexene, Argon atmosphere, RT, Specified time. b) As determined by GC-MS analysis

5. NMR Characterization data

5.1 Isolation of cyclooctylcyclooctene dimer: (IV,V) ¹H NMR (400 MHz) (CDCl₃): δ 1.2-2.12(m, 26H, H₃,H₄,H₅,H₆, H₂',H₃',H₄',H₅'); 2.2(m, 1H, H₁'); 5.3(m, 1H, H₂); ¹³C NMR (CDCl₃): δ 26.0, 26.1(C₄',C₅'); 26.5(C₃'); 26.8(C₆); 27.0(C₅); 28.5(C₄); 29.7(C₃); 32.0(C₂'); 45.8(C₁'); 121.5(C₂); 147.3(C₁). (E) ¹H NMR (400 MHz) (CDCl₃): δ 2.21(m, 8H, H_b); 1.62(m, 8H, H_c); 1.46(m, 12H, H_d,H_e). ¹³C NMR (CDCl₃): δ 26.3(C_d,C_e); 27.3(C_c); 31.2(C_b); 132.9(C_a). B.P. 150 °C.

Figure S38: ¹³C NMR spectroscopy of isolated cyclooctene dimer mixture containing (IV and V).

Figure S39: ¹H NMR NMR spectroscopy of isolated cyclooctene dimer mixture containing (IV and V).

Figure S40: ¹³⁵DEPT NMR spectroscopy of isolated cyclooctene dimer mixture containing (IV and V).

5.2 Isolation of 1-methylcyclohexene dimer mixture: (VI,VII). ¹³C NMR (CDCl₃): δ 54.7(C₁'); 122.8(C₂); 140.1(C₃). ¹³C NMR (CDCl₃): δ 54.7(C_a'); 119.6(C_b); 144.5(C_a). B.P. 75°C.

Figure S41: ¹³C NMR spectroscopy of isolated 1-methylcyclohexene dimer mixture (VI and VII) from FeCl₃ reaction.

Figure S42: ¹³⁵Dept NMR spectroscopy of isolated 1-methylcyclohexene dimer mixture (VI and VII)

5.3 Isolation of 3-methyl-1-(2-methylcyclohexyl)cyclohexene dimer (VII) dimer: ¹H NMR (400 MHz) (CDCl₃): δ 1.15-1.52 (m,14H, H_{b'}, H_{c'}, H_{d'}, H_e, H_f), 1.65(m, 2H, H_c, H_{f'}), 2.1(m, 1H, H_{a'}), 5.4(d, 1H, H_b). ¹³C NMR (CDCl₃): δ 16.1(C_{g'}); 16.8(C_g); 22.2-30.3(C_{b'}, C_{c'}, C_{d'}, C_{e'}, C_d, C_e, C_f); 35.1(C_{f'}, C_c); 54.7(C_a'); 119.6(C_b); 144.4(C_b).

Figure S43: ¹H NMR spectroscopy of isolated 3-methyl-1-(2-methylcyclohexyl)cyclohexene dimer (VII).

Figure S44: ¹³C NMR spectroscopy of isolated 3-methyl-1-(2-methylcyclohexyl)cyclohexene dimer (VII).

Figure S45: ¹³⁵DEPT NMR spectroscopy of isolated 3-methyl-1-(2-methylcyclohexyl)cyclohexene dimer (VII).

5.4 Isolation of 3-(2-phenylcyclohexyl)biphenyl (X): ¹H NMR (400 MHz) (CDCl₃): δ 1.58, 1.98(t, 4H, H_h); 1.73, 2.06(t, 4H, H_g); 2.85(t, 2H, H_e,H_f); 7.04-7.48(m, 14H, H_l,H_m,H_n,H_o,H_i,H_j,H_k,H_p,H_q,H_r). ¹³C NMR (CDCl₃): δ 26.8(Ch); 35.6(Cg); 50.6(Ce,Cf); 124.6, 125.7, 126.6, 126.9, 127.0, 127.2, 127.7, 128.1, 128.4, 128.7(C_l,C_m,C_n,C_o,C_i,C_j,C_k,C_p,C_q,C_r); 140.5(C_d); 141.6(C_c); 145.6(C_b); 146.0(C_a).

Figure S46: ¹³C NMR spectroscopy of isolated 3-(2-phenylcyclohexyl)biphenyl (X)

Figure S47: ¹H NMR spectroscopy of isolated 3-(2-phenylcyclohexyl)biphenyl (X)

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

Figure S48: Dept 135 NMR spectroscopy of isolated 3-(2-phenylcyclohexyl)biphenyl (X)

5.5 Isolation of bis(cyclooctyl): (XIII) ¹H NMR (400 MHz) (CDCl₃): δ 1.2(m, 2H, H₁); 1.3(m, 8H, H₃);

1.4(m, 8H, H₂); 1.5(m, 4H, H₅); 1.7(m, 8H, H₄). ¹³C NMR (CDCl₃): δ 26.7(C₃); 26.8(C₄); 26.9(C₅); 44.2(C₁).

Figure S49: ¹³C NMR spectroscopy of isolated bis(cyclooctyl) (XIII).

Figure S50: ¹H NMR spectroscopy of isolated bis(cyclooctyl) (XIII)

Figure S51: Dept 135 NMR spectroscopy of isolated bis(cyclooctyl) (XIII)

5.6 Isolation of bis(cyclohexyl): (XI) ¹H NMR (400 MHz) (CDCl₃): δ 0.94, 1.62(m, 8H, H₂); 1.03(m, 2H,

H₁); 1.18(m,4H, H₄); 1.7(m, 8H, H₃). ¹³C NMR (CDCl₃): δ 26.9(C₃,C₄); 30.2(C₂); 43.5(C₁).

Figure S52: ¹³C NMR spectroscopy of isolated bis(cyclohexyl) (XI)

Figure S53: ¹H NMR spectroscopy of isolated bis(cyclohexyl) (XI).

Figure S54: ¹³⁵DEPT NMR spectroscopy of isolated bis(cyclohexyl) (XI).

5.7 Isolation of Phenylcyclohexane: (VIII) ¹H NMR (400 MHz) (CDCl₃): δ 1.25(t, 2H, H₈); 1.42(m, 4H, H₇); 1.87(m, 4H, H₆); 1.18(t,1H, H₅); 7.15-7.29(m, 5H, H₂,H₃,H₄). ¹³C NMR (CDCl₃): δ 26.16(C₈); 26.90(C₇); 34.44(C₆); 44.58(C₅); 125.73(C₄), 126.78(C₂); 128.23(C₃); 148.03(C₁).

Figure S55: ¹H NMR spectroscopy of isolated phenylcyclohexane

5.8 Isolation of 1-cyclohexylcyclohexene dimer (I) : ¹H NMR (400 MHz) (CDCl₃): δ 1.1(m,2H, H_{2'},H_{6'}); 1.22(m, 2H, H_{3'},H_{5'}); 1.23(m, 2H, H₆); 1.59(m, 4H, H₄,H₅); 1.69(m, 2H, H_{2'},H_{6'}); 1.72(m, H, H_{1'}); 1.74(m, 2H, H_{3'},H_{5'}); 1.91(m, 2H, H_{4'}); 1.77(m, 2H, H₃); 5.3(s, 1H, H₂). ¹³C NMR (CDCl₃): δ 22.8, 23.2(C₄, C₅); 25.2(C₃); 26.5(C₆); 26.7(C_{4'}); 26.8(C_{3'},C_{5'}); 31.9(C_{2'},C_{6'}); 45.8(C_{1'}); 118.6(C₂); 143.1(C₁). B.P. 90^oC.

Figure S58: ¹H NMR spectroscopy of isolated 1-cyclohexylcyclohexene dimer (I)

Figure S59: ¹³⁵Dept NMR spectroscopy of isolated 1-cyclohexylcyclohexene dimer (I)

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