

1 PROCESS FOR DIMERIZING OLEFINS

2 FIELD OF THE INVENTION

3 The present invention relates to the dimerization of alpha-olefins by catalyzing
4 with a transition metal complex and a co-catalyst.

5 BACKGROUND OF THE INVENTION

6 Current alpha-olefin production processes yield large molar quantities of
7 1-butene, which has limited value. Thus, ways to avoid making 1-butene or to
8 convert 1-butene into higher value products are desired. Catalysts have been
9 used to dimerize 1-butene to octenes, but the selectivity of the catalysts for
10 the more desired linear internal octene isomers is low, and the activity and
11 conversion of the catalysts are low as well. A catalyst that is active and
12 selective for dimerization is desired. The products may be used as
13 precursors for production of plasticizers. Since 1-pentene, 1-hexene and
14 1-octene are also low molecular weight alpha olefins; they can also be
15 dimerized for making linear internal olefin dimers.

16 Currently, vinylidenes can be produced using triisobutylaluminum to catalyze
17 alpha olefin dimerization. In one embodiment, the reaction can use
18 0.5 weight percent triisobutylaluminum, take 4 to 6 hours, and be conducted
19 at 170 to 220°C. Under these conditions, the reaction gives approximately
20 70 percent alpha olefin conversion. The converted product includes 80 to
21 90 weight percent vinylidene and 10 to 20 weight percent internal dimer
22 olefins. Such a process is severely limited by high vinylidene olefin
23 selectivity. Additional process disadvantages include a long reaction time and
24 a high thermal requirement.

1 Alpha olefin dimerization technology to produce vinylidenes is known. In a
2 preferred embodiment, the catalyst used in the technology is composed of
3 bis(cyclopentadienyl)zirconium dichloride and an alumoxane in a molar ratio
4 of 1:4 at a 1000:1 olefin:aluminum molar ratio at 40°C. Under these
5 conditions, the reaction gives 93 percent alpha-olefin conversion in two hours.
6 The converted product includes 95 weight percent dimer olefin and only
7 2 weight percent internal olefins. A disadvantage of this catalyst system is
8 that it produces very little internal olefins. With proper catalyst selection, even
9 under the most reasonable conditions, the internal olefin selectivity would still
10 not make it economically feasible as a means of producing internal olefins.

11 The use of an alkylaluminum catalyst, 1 to 4 mole percent, at 100 to 140°C
12 has been disclosed. Specifically, the use of trioctylaluminum as the catalyst
13 is disclosed. In a preferred embodiment of the patent, the catalyst
14 concentration is 1.7 mole percent at 120°C. Under these conditions, the
15 reaction gives a 90 percent alpha olefin conversion in 192 hours. The
16 converted product includes 99 weight percent alpha olefin dimers, 95 weight
17 percent vinylidene, and only 4 percent internal dimer olefins. Though the
18 patent technology offers good dimer olefin selectivity, this patent does not
19 represent an efficient manufacturing process due to the long reaction times
20 and production of vinylidene olefins. Reaction times could be reduced by
21 increasing the alkylaluminum catalyst concentration, increasing the reaction
22 temperature, or reducing the conversion goal to less than 90 percent
23 conversion. However, the reaction times would still be too long to provide a
24 reasonable manufacturing process.

25 A catalyst system composed of bis(cyclopentadienyl)-zirconium dichloride, an
26 aluminoxane other than methylaluminoxane (all examples use
27 isobutylaluminoxane), and trimethylaluminum has also been disclosed. In a
28 typical example, the catalyst system is approximately 7.5 mmoles aluminum

1 (3.9 mmoles aluminoxane and 3.7 mmoles trimethylaluminum) and
2 0.11 mmoles of bis(cyclopentadienyl)zirconium dichloride and reacts with
3 128 mmoles of olefin at 50°C. Under these conditions, the catalyst gives a
4 92.7 percent alpha olefin conversion in six hours. The converted product
5 includes 90 weight percent dimer vinylidene olefin and only 7 weight percent
6 internal olefin. This system also has the disadvantage of producing
7 vinylidene olefins and not enough internal olefins.

8 A method of manufacturing alpha-olefins by contacting ethylene with an iron
9 complex of a selected 2,6-pyridinedicarboxaldehyde bisimine or a selected
10 2,6-diacylpyridine bisimine is also known. Although the catalysts used in this
11 method are closely related to the catalysts used in the present invention, this
12 method has not been connected with the dimerization of olefins. Rather, this
13 method deals with the manufacture of alpha-olefins from ethylene.

14 In contrast, Applicants have achieved a process of dimerizing α -olefins using,
15 as a pre-catalyst, a tridentate bisimine ligand coordinated to an iron center.
16 This pre-catalyst is activated by the addition of a co-catalyst, which may be an
17 alumoxane or a combination of a Lewis acid and an alkylating agent. Once
18 activated, the catalyst dimerizes α -olefins rapidly to form a mixture of linear,
19 internal olefin dimers and methyl-branched internal olefin dimers.

20 SUMMARY OF THE INVENTION

21 The invention relates to a method of making olefin dimers and method of
22 using a transition metal complex to dimerize alpha-olefins comprising the
23 steps of:

- 24 (a) Adding to a container under inert gas atmosphere a catalyst comprising
25 a transition metal complex;
- 26 (b) Adding alpha-olefin monomer to the container with the catalyst;

1 (c) Adding to the container with the monomer and pre-catalyst an activating
2 co-catalyst; and

3 (d) Forming a linear internal olefin dimer mixture comprising linear internal
4 olefin dimers and methyl-branched internal olefin dimers.

5 A preferred embodiment of the invention is a process for dimerizing at least
6 50 mole percent of an alpha-olefin monomer at a selectivity of at least
7 60 mole percent to linear internal olefin dimers. In a more preferred
8 embodiment, at least 90 mole percent of the olefin dimer mixture is linear
9 olefin or methyl-branched olefin.

10 BRIEF DESCRIPTION OF THE DRAWING

11 The figure is a graph plotting the % linear internal olefin dimers vs. the
12 temperature at which the reaction is run. Dimerization of both C₆ and C₄ is
13 plotted using Catalyst 1.

14 DETAILED DESCRIPTION OF THE INVENTION

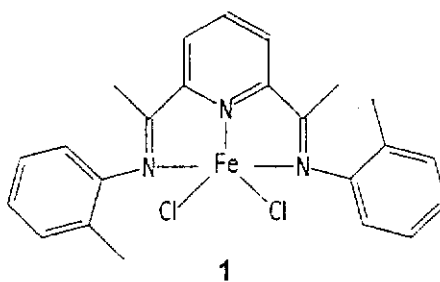
15 Alpha-olefins that can be used in the process include straight chain terminally
16 unsaturated monoolefinic aliphatic hydrocarbons. Preferred alpha-olefins are
17 those containing at least 4 and up to 36 or more carbon atoms. Most
18 preferred alpha-olefins are 1-butene, 1-pentene and 1-hexene or a mixture of
19 the group consisting of 1-butene, 1-pentene, 1-hexene and 1-octene.

20 Any transition metal complex with a co-catalyst may be used as a catalyst in
21 the process. In a preferred embodiment, the activating co-catalyst may be
22 alumoxane or a combination of a Lewis acid and an alkylating agent.

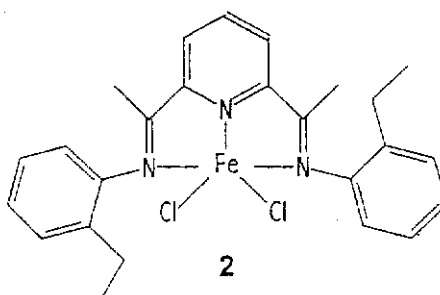
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- 1 The preferred transition metal complexes are tridentate bisimine ligands
- 2 coordinated to an iron center or a combination of an iron center and aryl rings,
- 3 either substituted or unsubstituted.

- 4 The most preferred transition metal complexes are selected from the group
- 5 consisting of catalysts 1, 2, 3, 4 and 5:

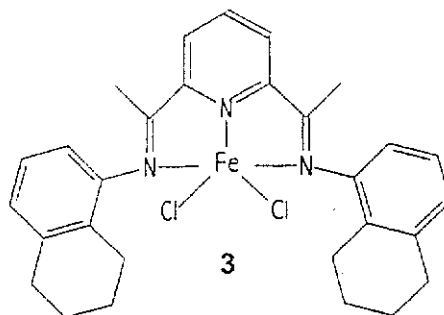


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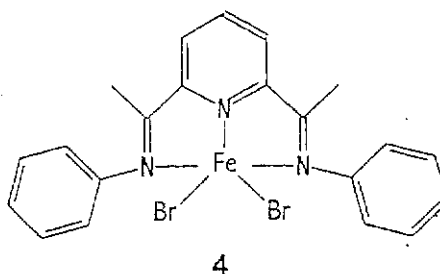


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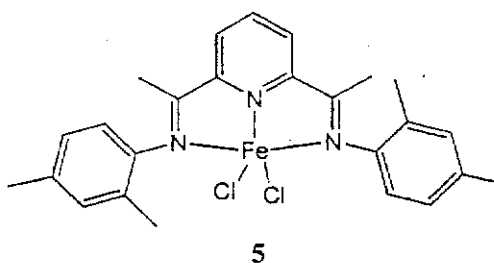
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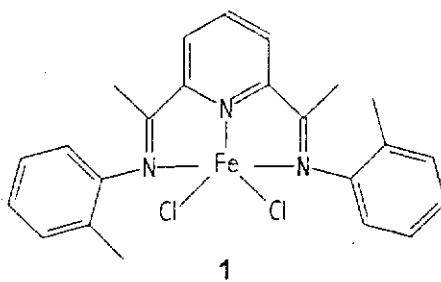


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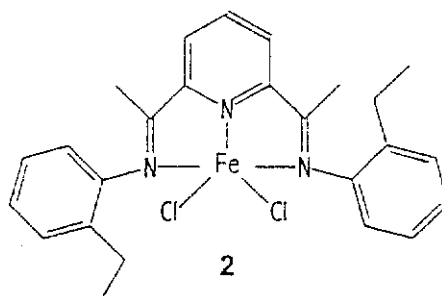
- 4 The effective amount of transition metal complex catalyst is quite low. With
5 the catalyst and co-catalyst less than 1% by mass of the total alpha-olefin
6 mixture, the dimerization reaction occurs in minutes.
- 7 A preferred catalyst concentration is 0.01-0.1 mg of catalyst per ml of
8 alpha-olefin monomer. A more preferred catalyst concentration is
9 0.02-0.08 mg of catalyst per ml of alpha-olefin monomer. An even more

- 1 preferred catalyst concentration is 0.05 to 0.06 mg of catalyst per ml of
2 alpha-olefin monomer.
- 3 Preferred co-catalysts are selected from the group consisting of an
4 alumoxane or a combination of a Lewis acid and an alkylating agent. A
5 preferred co-catalyst is methylaluminumoxane (MMAO) in molar excess.
- 6 The following observations can be made about the reaction:
- 7 (1) The reaction proceeds more rapidly in neat α -olefin than in solution.
- 8 (2) The reaction initiated by addition of the co-catalyst can be conducted at
9 a temperature in a range of from 0°C to 85°C. The reaction proceeds
10 more rapidly at elevated temperatures (30-70°C). These temperatures
11 are obtained by activating the reaction at room temperature and allowing
12 the reaction exotherm to heat the solution.
- 13 (3) Conversion is limited by the decreasing concentration of substrate
14 available. As the amount of dimer is increased, the concentration of
15 α -olefin decreases. This may lead to catalyst deactivation.
- 16 There were two general procedures used for the dimerization experiments,
17 with the difference depending on the nature of the substrate. For monomers
18 that are liquids at standard atmospheric conditions, benchtop experiments
19 were carried out using standard Schlenk line techniques to exclude excess
20 moisture and air. For butene, the experiments were performed in a 500 ml
21 Zipperclave reactor in liquid butene. The catalysts 1, 2, 3, 4 and 5 used are
22 shown below.

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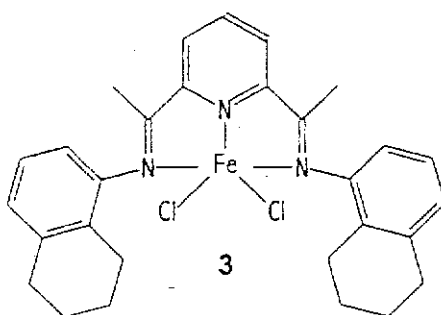


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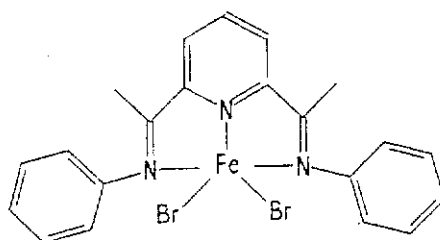
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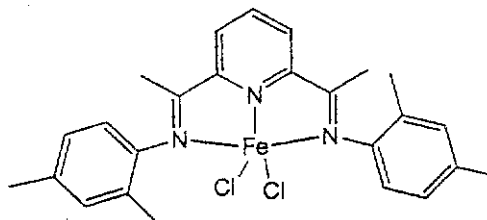


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Dimerization Method 1

Dimerization of 1-hexene and liquid monomers

A two-necked flask with a stirbar was fitted with a reflux condenser on one neck and a thermocouple with the appropriate adapter on the other neck. The setup was heated under vacuum via the insertion of a needle in the septum at the top of the condenser. After heating, the setup was back-filled with nitrogen from the Schlenk manifold. The condenser was then removed under positive nitrogen flow and the pre-catalyst was added quickly. After replacing the condenser, the flask was back-filled three times with nitrogen and charged with the liquid monomer. In the cases of 1-hexene, the monomer was a commercial grade of Chevron Chemical's Gulftene-6. The monomer was used "as is". Stirring was begun in order to effectively slurry the sparingly soluble catalyst in the neat monomer. After several minutes, the co-catalyst was added via syringe. All of the reactions were activated at room

1 temperature or lower, but the exothermic nature of the reaction caused the
2 temperature in many cases to rise significantly. These temperatures were
3 monitored using the thermocouple, and the temperatures listed in the table
4 represent the maximum temperatures achieved in the reaction. In some
5 cases, the exotherm was controlled by a water bath. After reaching the
6 maximum temperature in each reaction, a cooling process was observed.
7 This cooling does not necessarily indicate that the catalyst is becoming
8 deactivated. It is quite likely a feature of the reaction kinetics, meaning that
9 as the substrate is consumed, the heat of reaction per unit time begins to
10 decrease accordingly. Examples 1 to 3, 5 to 8 and 10 to 18 of Table 1 were
11 made using Dimerization Method 1.

12 Dimerization Method 2

13 Dimerization of 1-butene

14 A 500 ml Zipperclave reactor was heated under vacuum at 50°C for several
15 hours. The reactor was cooled to room temperature under nitrogen. The
16 pre-catalyst was then quickly added to the reactor, and the reactor was
17 resealed and placed under vacuum. A dual-chambered glass sample charger
18 was then attached to the injection port of the reactor. From the first chamber,
19 a small amount of cyclohexane (usually about 20 ml) was added. From the
20 second chamber, more cyclohexane (usually about 10 ml) and the co-catalyst
21 were added. The total amount of cyclohexane was carefully measured. The
22 reactor was then quickly sealed and charged with 200 ml of liquid butene.
23 The reactor was further pressurized with at least 100 psi of nitrogen to help
24 keep the butene in the liquid phase. The reaction was stirred rapidly, and the
25 temperature was monitored using a thermocouple. Exotherms due to the
26 heat of reaction were observed, and the reaction temperatures listed
27 correspond to the maximum temperatures observed in the reactions.
28 Examples 4 and 9 of Table 1 were made using Dimerization Method 2.

Product Analysis Method

General Procedure for Analyzing Reaction Product

The aluminum co-catalysts were removed by pouring the liquid products into a water wash. After removal of the co-catalysts, the products were analyzed by gas chromatography (GC). GC analysis showed clear separation of the linear from the branched species, and hydrogenation of the products confirmed these results. The percentages of linear vs branched materials in the products were usually determined from the hydrogenation data, but it was often possible to determine these numbers accurately without hydrogenation. ^{13}C NMR and ^1H NMR were used to confirm the internal olefin content in the products, with only about 1% of vinylidene products present. The Figure is a plot constructed to show the selectivity for linear internal species for catalyst 1 with changes in temperature. Note that while the activity and the conversion of the catalyst decreases with decreasing temperature, the selectivity for internal olefins increases. Based on Example 13 in the Table 1, it appears that 40°C may be the optimum temperature for running these reactions. Also, note from the plot that the selectivity for linear internal products does not depend on the monomer.

The conversions and yields were determined by comparing the product peaks to internal standard peaks, and by assuming equal response factors of the standards and the products. For the hexene dimerization experiments, 1-hexene was the internal standard, and for the butene experiments cyclohexane was used. The butene conversion levels are approximate because the exact density of butene under the reaction conditions is not known.

Table 1, below, collects the data from 18 experiments, fifteen experiments (Examples 1, 2, 3, 5, 6, 7, 8, 10, 11, 12, 13, 14, 15, 16 and 18) performed with the hexene monomer according to Dimerization Method 1, two

1 experiments (Examples 4 and 9) performed with the butene monomer
2 according to Dimerization Method 2, and one experiment (Example 17)
3 performed with both pentene and hexene monomer according to Dimerization
4 Method 1. Table 1 describes the various conditions used including which of
5 the five catalysts were used.

Table 1

Ex.	Catalyst	Loading (mg)	Co-catalyst	Loading	α -olefin monomer	Amount (ml)	React. length	React. temp. (°C)	% conv.	Yield (g)	TON	% dimer	% linear Internal	% methyl branched
1	1	6.0	MMAO, 6.42% Al	2.0 ml	C6	20	10 min	-65°C	55	7.4	6,800	92	64	35
2	1	1.0	MMAO, 6.42% Al	1.0 ml	C6	20	3h	25	21	2.8	15,600	92	76	23
3	1	1.0	MMAO, 6.42% Al	1.0 ml	C6	20	3h	0	9	1.2	6,700	85	81	18
4	1	5.1	MMAO, 6.42% Al	3.5 ml	C4	200	1h	30	~22	26.0	42,600	85	71	28
5	2	5.9	MMAO, 6.42% Al	3.0 ml	C6	50	1h	~30	28	9.4	9,400	87	71	28
6	1	11.7	MMAO, 6.42% Al	6.0 ml	C6	200	2h	65	29	39.3	18,700	85	63	36
7	3	5.8	MMAO, 6.42% Al	3.0 ml	C6	100	15 min	53	26	17.6	19,400	90	70	29
8	4	10.7	MMAO, 6.42% Al	4.0 ml	C6	100	30 min	82	58	39.2	23,100	96	27	70
9	1	10.0	MMAO, 6.42% Al	3.0 ml	C4	200	1h	40	~58	70.6	59,000	83	71	28
10	4	4.3	MMAO, 6.68% Al	3.0 ml	C6	100	2h	20	8	5.6	8,200	95	34	65
11	4	6.0	MMAO, 6.68% Al	3.0 ml	C6	100	1h	50	44	29.8	31,300	96	29	70
12	2	10.5	MMAO, 6.68% Al	3.0 ml	C6	100	4h	30	16	10.8	6,100	86	69	30

13	1	10.5	MMAO, 6.68% Al	6.0 ml	C6	200	5h	40	70	93.9	49,800	83	66	33
14	5	10.5	MMAO, 6.68% Al	6.0 ml	C6	200	1h	40	64	86.1	48,400	85	65	34
15	5	6.8	MMAO, 6.68% Al	3.0 ml	C6	100	2h	0	33	22.3	19,400	83	80	19
16	5	5.9	MMAO, 6.68% Al	3.0 ml	C6	100	1h	40	68	43.8	52,600	86	66	33
17a	5	6.3	MMAO, 6.68% Al	3.0 ml	C5, C6	47, 53	1h	40	65	42.8	43,700	85	64	35
18	3	5.5	MMAO, 6.68% Al	3.0 ml	C6	100	1h	40	36	24.1	28,600	90	71	28

- 1 (a) Co-dimerization using 1-pentene and 1-hexene in equimolar amounts. GC analysis revealed that equimolar amounts ($\pm 5\%$) of each monomer were
- 2 incorporated into the resultant dimers and trimers.

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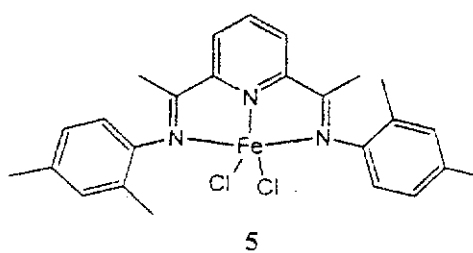
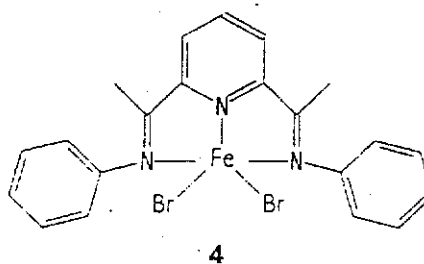
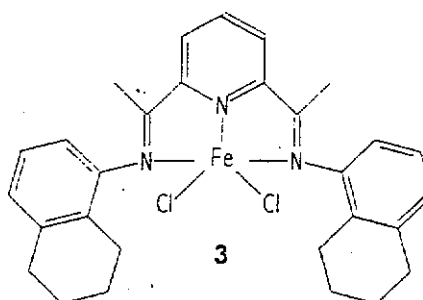
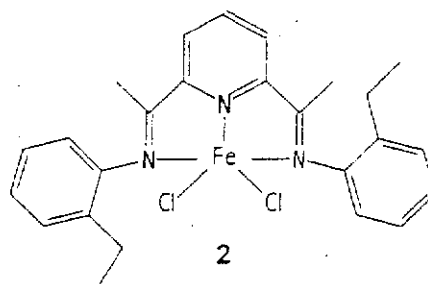
- 1 While the present invention has been described with reference to specific
- 2 embodiments, this application is intended to cover various changes and those
- 3 skilled in the art may make those substitutions without departing from the
- 4 spirit and scope of the appended claims.

Claims

1. A method of making internal olefin dimers comprising the steps of:
 - (a) adding to a container under inert gas a pre-catalyst comprising a transition metal center complexed with a tridentate bisimine ligand bearing substituted or unsubstituted aryl rings;
 - (b) adding alpha-olefin monomer to the container with the pre-catalyst;
 - (c) adding to the container with the monomer and pre-catalyst an activating co-catalyst; and
 - (d) forming an olefin dimer mixture comprising linear olefin dimers and methyl branched olefin dimers.
2. The method of claim 1 wherein at least 50 mole percent of the alpha-olefin monomer is dimerized to internal olefin dimer.
3. The method of claim 1 wherein at least 90 mole percent of the olefin dimer mixture is linear olefin or methyl-branched olefin.
4. The method of claim 2 wherein at least 60 mole percent of the internal olefin dimer is linear internal olefin dimer.
5. The method of claim 1 wherein the transition metal center is iron.
6. The method of claim 1 wherein the concentration of the transition metal catalyst is in a range from 0.01 to 0.1 mg catalyst per ml of alpha-olefin monomer.

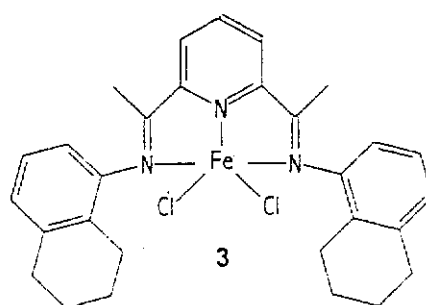
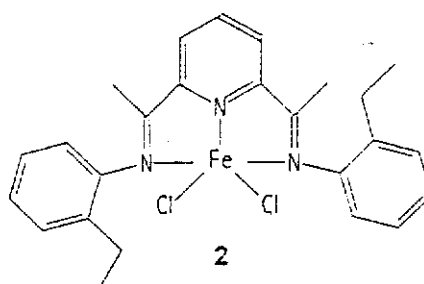
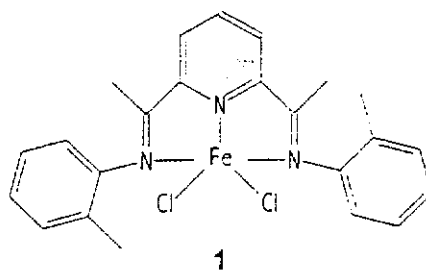
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12. The method according to claim 1 wherein the alpha-olefin monomer is selected from the group consisting of normal alpha-olefin chains having from 4 to 36 carbon atoms.
13. The method according to claim 12 wherein the alpha-olefin monomer is selected from the group consisting of 1-butene, 1-pentene and 1-hexene.
14. The method according to claim 12 wherein the alpha-olefin monomer is a mixture of at least two of the group consisting of 1-butene, 1-pentene, 1-hexene and 1-octene.
15. The method according to claim 1 wherein the addition of activating co-catalyst in step (c) is conducted at a temperature in a range from 0°C to 85°C.
16. The method according to claim 15 wherein the addition of activating co-catalyst in step c) is conducted at a temperature in a range from 30°C to 85°C.
17. A method of using a transition metal complex as a catalyst to dimerize alpha-olefins comprising the steps of:
 - (a) adding to a container under inert gas a pre-catalyst comprising a transition metal center complexed with a tridentate bisimine ligand bearing substituted or unsubstituted aryl rings;
 - (b) adding alpha-olefin monomer to the container with the pre-catalyst;
 - (c) adding to the container with the monomer and pre-catalyst an activating co-catalyst; and

- (d) forming an olefin dimer mixture comprising linear olefin dimers and methyl branched olefin dimers.
18. The method of claim 17 wherein at least 50 mole percent of the alpha-olefin monomer is dimerized to internal olefin dimer.
 19. The method of claim 17 wherein at least 90 mole percent of the olefin dimer mixture is linear olefin or methyl-branched olefin.
 20. The method of claim 18 wherein at least 60 mole percent of the internal olefin dimer is linear internal olefin dimer.
 21. The method of claim 17 wherein the transition metal center is iron.
 22. The method of claim 17 wherein the concentration of the transition metal catalyst is in a range from 0.01 to 0.1 mg catalyst per ml of alpha-olefin monomer.
 23. The method of claim 22 wherein the concentration of metal catalyst is in a range from 0.02 to 0.08 mg catalyst per ml of alpha-olefin monomer.
 24. The method of claim 22 wherein the concentration of metal catalyst is in a range from 0.05 to 0.06 mg catalyst per ml of alpha-olefin monomer.
 25. The method of claim 17 wherein the catalyst and co-catalyst are less than 1% by mass of the alpha-olefin monomer in the container.
 26. The method of claim 17 wherein the activating co-catalyst is aluminumoxane or a combination of a Lewis acid and an alkylating agent.
 27. The method of claim 22 wherein the transition metal complex is selected from the group consisting of structures 1, 2, 3, 4 and 5:





28. The method according to claim 17 wherein the alpha-olefin monomer is selected from the group consisting of normal alpha-olefin chains having from 4 to 36 carbon atoms.
29. The method according to claim 28 wherein the alpha-olefin monomer is selected from the group consisting of 1-butene, 1-pentene and 1-hexene.
30. The method according to claim 28 wherein the alpha-olefin monomer is a mixture of at least two of the group consisting of 1-butene, 1-pentene, 1-hexene and 1-octene.
31. The method according to claim 17 wherein the addition of activating co-catalyst in step (c) is conducted at a temperature in a range from 0°C to 85°C.
32. The method according to claim 31 wherein the addition of activating co-catalyst in step (c) is conducted at a temperature in a range from 30°C to 85°C.