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Oligomerization of 1-butene with a homogeneous catalyst system based on allylic nickel complexes

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The oligomerization of 1-butene with a nickel-based catalyst system constitutes an elegant synthesis method for obtaining linear octenes from readily available chemicals. It is well known that the bis-(cyclooctadiene)nickel(0)-complex (Ni(COD)$_2$) can be used in combination with 1,1,1,5,5,5-hexafluoroacetylacetone (hfacac) forming **[Ni-1]** as a catalyst for the dimerization of 1-butene, which produces a linear octene yield of 75–83% at reaction temperatures between 70–80 °C. We are the first to demonstrate that it is also possible to use allylic nickel complexes in combination with hfacac to produce linear octenes with a selectivity of 70% under very mild reaction conditions and at low catalyst concentrations. Additionally the catalyst can be formed simply by adding the activator hfacac to a solution of the allylic nickel complex. No complicated synthesis or purification is needed.

Introduction

The oligomerization of short-chained olefins plays an important role in the chemical industry. Linear olefins with a chain length of C_6–C_{10} are highly desired intermediates. For example, after hydroformylation and the subsequent hydrogenation of the aldehydes to the alcohols, they can be used as plasticizers for polyvinylcloride as phthalic acid esters. Another major application of octenes is the use as a comonomer in the production of linear low density polyethylene (LLDPE).[5] As longer chained linear olefins cannot be produced *via* conventional crack processes, industrial processes exist which allow them to be generated *via* the homogenous and heterogeneous metal-catalyzed oligomerization of C_2–C_4 alkenes.

In heterogeneous processes the catalyst is typically immobilized on a supporting material. Acid compounds such as zeolites or phosphoric acid on supporting materials are an example of heterogeneous catalysts (*e.g.* SiO_2). The main problem with these catalysts is that their oligomerization products are very highly branched yielding 3,5-dimethylhexenes as he major product.[6–9] A heterogeneous catalyzed non-acidic oligomerization of alkenes is carried out in *Evonik Industries' OCTOL* process, in which nickel supported catalysts are used. The advantage of this process is that the formation of branched alkenes could be reduced due to the low acidity of the catalyst system. However, the main products of the butene oligomerization are the mono-branched dimers, the methyl heptenes.[6,10,11]

Another efficient method to oligomerize low chained alkenes are homogenous catalyzed processes. One of the most important homogenous oligomerization processes is the *DIMERSOL* process, which was developed by the *Institut Français du Pétrole (IFP)* in the 1970s. This alkene oligomerization is run with a nickel complex, which is activated by an aluminum alkyl compound. As the nickel catalyst cannot be separated, it is deactivated with an ammonia solution. Anyway, the linear octene yield is only 6%.[12–18]

With the development of the *DIFASOL* process, recycling the catalyst became possible by running the reaction in a liquid–liquid two phase system. The system consists of an ionic liquid as a solvent for the catalyst and as a co-catalyst, and a non-polar product phase. But the linear octene yield is with this process very low, too.[14–20]

As opposed to these processes, the Ni(H-COD)(hfacac) **[Ni-1]**, which was developed by Keim *et al.*, leads to a 70–80% yield of linear dimers in the oligomerization of 1-butene.[1–4] Another difference in the above-mentioned processes is that the catalytic active species is not generated *via* the interaction of nickel^{II} with a Lewis acid, but *via* a β-hydride elimination, which forms a nickel-hydride (Fig. 1). The absence of a Lewis acid and thus of acid centers allows the linear oligomerization of alkenes. They also find out that diketones with electron withdrawing effects are more effective for the activation of the nickel(0). Especially 1,1,1,5,5,5-hexafluoroacetylacetone (hfacac) lead to a high catalyst activity.[1–4]

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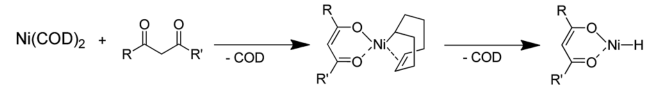

Fig. 1 Forming of the nickel hydride spezies.

A similar and highly active catalyst for the oligomerization of alkenes was described by *Wilke et al.*[21] *Wilke* was able to synthesize an allylic nickel complex for the oligomerization of propene. The catalyst system consists of an allylic nickel complex, an aluminum alkyl and a phosphine ligand (Fig. 2).[20–22]

Due to the presence of aluminum alkyls, the oligomerization of propene yields 70–80% 2-methylpentenes, 5% 2,3-dimethylbutenes and only 10–20% *n*-hexenes.

The activation of the methallyl nickel chloride dimer **[Ni-2]** with hfacac was investigated for the first time in this paper. By using hfacac instead of aluminum alkyls a high linear octene formation was intended (Fig. 3).

Results and discussion

To investigate how allylic nickel complexes catalyze the dimerization of alkenes, a stoichiometric reaction of the **[Ni-2]** complex and 1-hexene was carried out at 30 °C. After 24 h reaction time and analysis *via* GC-MS, a signal of 138 [Da] was detected, which coincides with the molar weight of the co-dimer of 1-hexene and the methallyl ligand. Therefore, we postulate that the catalytic active nickel hydride species was formed by the addition of the methallyl ligand to 1-hexene (steps **B–C**) and a subsequent β-hydride elimination (step **D**). Because of the instability of these intermediates an isolation was not possible (Fig. 4).

This shows that it is not necessary to use the zero valent, highly moisture and oxidation sensitive Ni(COD)$_2$ precursor. The new catalyst system is active already at the very low temperature of 30 °C.

The oligomerization occurred in a manner similar to the typical oligomerization mechanisms (steps **E–I**) or (steps **E–J**) after the activation of the catalyst:

E: coordination of an alkene
F: hydride addition
G: coordination of a second alkene
H: alkene insertion
I: β-hydride elimination, or
J: trimerization by addition of another alkene.

The oligomerization of 1-butene leads to the formation of different octenes. Among the major and industrially most desired isomers are the linear octenes. Other isomers that occur include the branched dimers 2-ethylhex-1-ene, 3-methylheptenes and 2-ethyl-3-methylpent-1-ene. A key reason for the formation of branched dimers is that 1-butene dimerization can occur by different means of insertion. A constellation of all possible means of insertion are summarized in Fig. 5, which clearly depicts how the formation of linear octenes is only possible by the insertion pathway **AB**. Another reason for the formation of branched dimers is the inevitable isomerization of 1-butene to 2-butenes, which only leads to the formation of branched dimers.

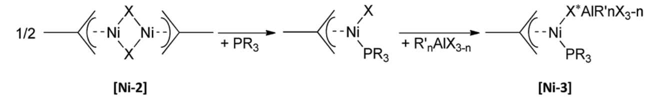

Fig. 2 Synthesis of the *Wilke*-catalyst [Ni-3].

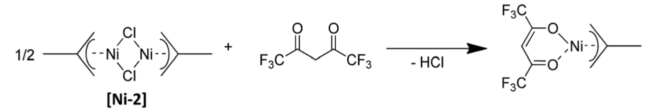

Fig. 3 Forming of the catalyst from an allylic nickel complex and hfacac.

Since these isomers are very complex to separate *via* gas chromatography, a hydrogenation to the saturated compounds were carried out. After hydrogenation there arise only the following octane isomers: the *n*-octane and the branched isomers 3-methylheptane and 3,5-dimethylhexane.

Activator screening

The activator is crucial to this reaction, as it leads to the formation of the catalytic active nickel hydride species and increases the catalyst activity of the allylic nickel complex. For this purpose, the oligomerization of 1-butene was carried out with different Lewis or Brønsted acids, each of which were investigated at 30 °C and 1 mol% of **[Ni-2]** with dichlormethane (dcm) as solvent (Fig. 6). After 24 h reaction time, the highest yield of 41% dimers (C_8) was observed with hfacac. In comparison, the Lewis acids $BF_3 \cdot OEt_2$, $SnCl_2 \cdot 2H_2O$ and $FeCl_3$ yielded approximately 10–20%. A comparable oligomerization activity but low dimer (7%) and higher trimer (C_{12}) yield (21%) was obtained with NH_4BF_4. Only $AlClEt_2$ and $AlCl_2Et$ led to a deactivation of the catalyst.

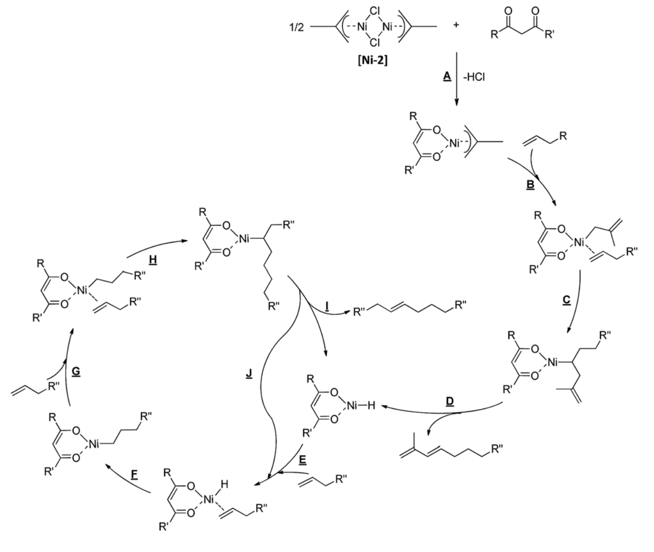

Fig. 4 Postulated mechanism of the oligomerization of 1-butene with an allylic nickel complex and a diketone as an activator.

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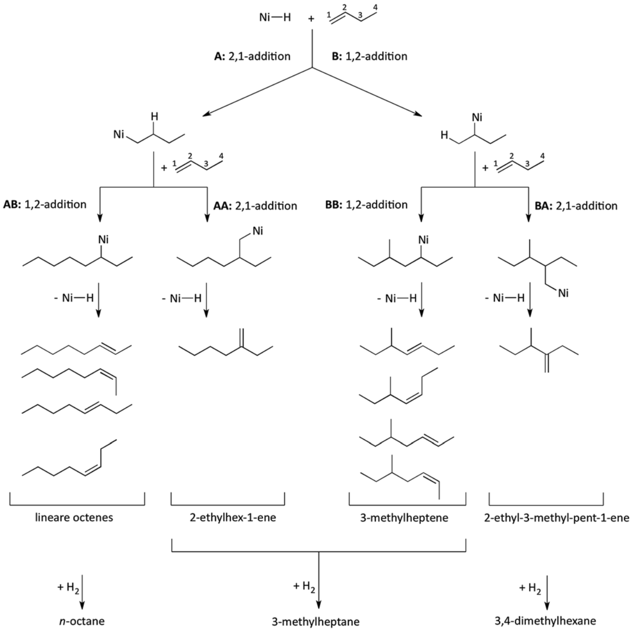

Fig. 5 Possibilities of inserting 1-butene in oligomerization reactions with catalytic active nickel hydrides.

Similar activity was observed when comparing the oligomerization activity of **[Ni-2]** to the Ni(H-COD)(hfacac) **[Ni-1]**. Whereas **[Ni-2]** was active at reaction temperatures as low as 30 °C, the **[Ni-1]** complex had very low activity under 70 °C. The dimer yield with the **[Ni-1]** complex was 41% at a reaction temperature of 70 °C.

In order to determine the percentage of linear octenes between the produced dimers, the reaction mixture with hfacac was hydrogenated at 80 °C and 30 bar hydrogen with the *Wilkinson*-catalyst $RhCl(PPh_3)_3$. The results show that the allylic nickel complex **[Ni-1]** leads to a high linear octene yield of 70%.

Influence of the reactant concentration

As the concentration of the reactant 1-butene in the reaction mixture plays an important role, different w(dcm)/w(1-butene)-ratios were investigated. The results in Fig. 7 show that a low 1-butene concentration led to low dimer yields. The thinning of the solution lead to a decrease of the 1-butene molecule collusions. A high dimer yield of 61 or 67% was obtained with a w(dcm)/w(1-butene)-ratio of 1 or 2, in which a w(dcm)/w(1-butene)-ratio of 1 led to a higher trimer yield of 21%. The reason for that is the increasing collisions frequency of 1-butene and the dimer with decreasing concentrations of the solvent.

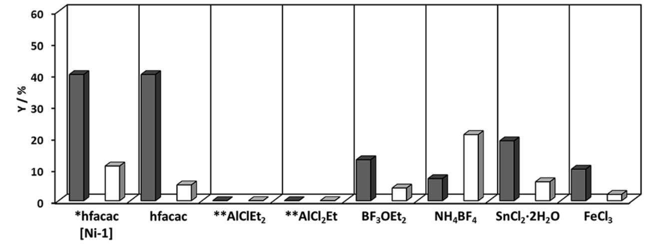

Fig. 6 Results of the activator screening (c([**Ni-2**]) = 1 mol%, n(activator)/n([**Ni-2**]) = 1, rt = 24 h, solvent = dcm, w(solvent)/w(1-butene) = 5, $T = 30$ °C, Y_{4a-d} = yield of dimers and trimers determined by GC; * = [**Ni-1**], $T = 70$ °C, solvent = toluene; ** = solvent toluene; ■ $Y(C_8)$, □ $Y(C_{12})$).

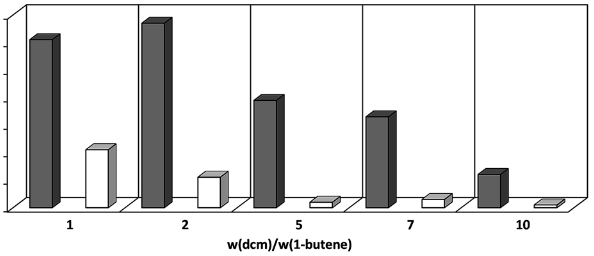

Fig. 7 Variation of the w(dcm)/w(1-butene)-ratio (c([**Ni-2**]) = 1 mol%, n(hfacac)/n([**Ni-2**]) = 1, solvent = dcm, $T = 30$ °C, rt = 24 h, Y_{4a-d} = yield of dimers and trimers determined by GC; ■ $Y(C_8)$, □ $Y(C_{12})$).

Influence of the activator concentration

Another important factor is the n(hfacac)/n([**Ni-2**])-ratio, as described in the mechanistic study. To investigate the influence of the n(hfacac)/n([**Ni-2**])-ratio, reactions with different ratios were conducted. In previous reactions, an n(hfacac)/n([**Ni-2**])-ratio of 1 was used. The n(hfacac)/n([**Ni-2**])-ratio was varied between 0.1–1 and 1–10 (Fig. 8).

The results of these reactions show that a molar ratio of hfacac to [**Ni-2**] below and higher than 1 led to an decrease of the dimer yield. A reason for this decrease at low hfacac concentrations is that the activation of the nickel complex does not occur completely. In contrast, high concentrations of hfacac led to a blockage of the nickel center and so the 1-butene molecules cannot coordinate to the nickel. The highest yield of dimers (67%) was obtained at an n(hfacac)/n([**Ni-2**])-ratio of 1.

Solvent screening

The influence of the solvent was investigated, as the solvent can act as an activator or as a ligand for many transition metal catalysts. Fig. 9 shows the results of the solvent screening with different polar non-protic solvents. Non-protic solvents were investigated as allylic nickel complexes are stable in these solvents.

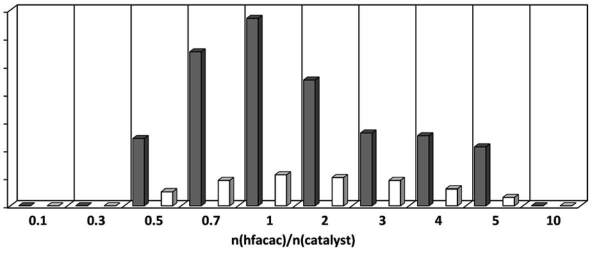

Fig. 8 Influence of the activator concentration (c([**Ni-2**]) = 1 mol%, solvent = dcm, w(solvent)/w(1-butene) = 2, $T = 30$ °C, rt = 24 h, Y_{4a-d} = yield of dimers and trimers determined by GC; ■ $Y(C_8)$, □ $Y(C_{12})$).

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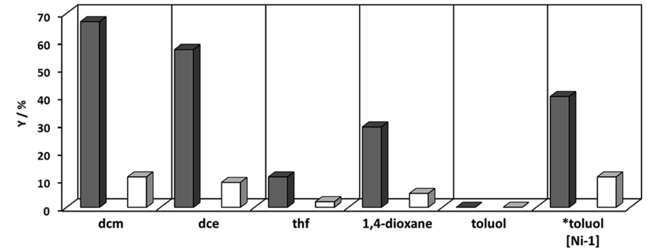

Fig. 9 Results of the solvent screening (c([**Ni-2**]) = 1 mol%, n(hfacac)/n([**Ni-2**]) = 1, w(solvent)/w(1-butene) = 2, $T = 30$ °C, rt = 24 h, Y_{4a-d} = yield of dimers and trimers determined by GC; * = [**Ni-1**], $T = 70$° C; ■ $Y(C_8)$, □ $Y(C_{12})$).

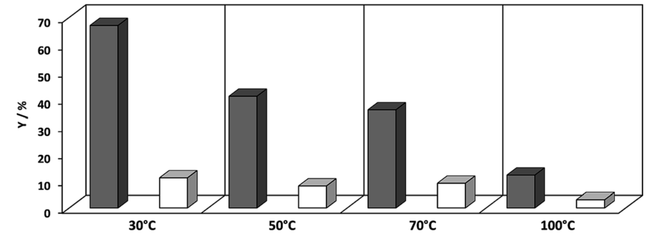

Fig. 10 Variation of the reaction temperature (c([**Ni-2**]) = 1 mol%, n(hfacac)/n([**Ni-2**]) = 1, rt = 24 h, solvent = dcm, w(solvent)/w(1-butene) = 2, Y_{4a-d} = yield of dimers and trimers determined by GC; ■ $Y(C_8)$, □ $Y(C_{12})$).

The highest yield of dimers (67% and 57%) was obtained with dichlormethane (dcm) and dichlorethane (dce) at 30 °C. It can be assumed that chlorinated solvents are advantageous for the oligomerization of alkenes with allylic nickel complexes, whereas coordinating solvents like thf or 1,4-dioxan led to a blockage of the catalyst. A remarkable difference in the catalyst activity of the [**Ni-1**] and allylic nickel complexes appeared with toluene as a solvent. A dimer yield of 40% was obtained with the [**Ni-1**] in toluene, whereas the allylic nickel complex had no activity in toluene.

Temperature screening

Temperature plays an important role in most chemical reactions because it provides the energy required to bridge the activation energy of the reaction. Furthermore, most homogenous transition metal complexes are not stable at high temperatures, thus the optimal temperature, at which the catalyst activity and stability are maximized, must be identified. For this purpose, the oligomerization of 1-butene was conducted at 5 different temperatures in dcm with 1 mol% of [**Ni-2**]. The results in Fig. 10 show that reaction temperatures over 30 °C led to a decrease in the dimer yield. In addition, a precipitation of nickel was observed at reaction temperatures over 70 °C.

Conclusion

We demonstrated that it is possible to use hfacac as an activator for allylic nickel complexes for the oligomerization of 1-butene. In addition, we observed that only the equimolar ratio of hfacac to [**Ni-2**] was optimal to achieve high catalyst activity. Chlorinated solvents were the most effective solvents at a w(solvent)/w(1-butene)-ratio of 2 for producing a high yield of the desired dimers. It was also necessary to use a mild reaction temperature near 30 °C to obtain high dimer yields of 67%. The trimers were built with only 21%. Finally, we were able to generate a catalyst complex that can dimerize 1-butene to the highly desired linear octenes at selectivities of 70%.

Experimental section

Typical oligomerization experiment

The oligomerization reactions were carried out using the general *Schlenk* method. All solvents were dried over mol sieves (4 Å) and degased. In a representative experiment, 0.1064 g of [**Ni-2**] (0.0356 mmol, 1 mol%) were dissolved in 4 g dichlormethane.

Then 0.0746 g hfacac (0.0356 mmol, 1 mol%) were added dropwise to the solution and stirred for 1 h. The solution turned from brown to red. Then the solution was transferred to an autoclave and 2 g of 1-butene were added. The reaction was analyzed with GC-FID to determine the dimer and trimer yields and GC-MS to characterize both compounds.

To determine the yield of linear dimers a hydrogenation of the reaction solution was carried out. This was necessary because the isomers could not be separated on our GC-column (30 m HP-5.5% phenylmethylsiloxane column). The hydrogenation takes place at a reaction temperature of 80 °C, 30 bar hydrogen with 1 mol% of the Wilkinson-catalyst $RhCl(PPh_3)_3$.

Product characterization. As the octene isomers could not be separated by column chromatography, a 1H-NMR spectrum of the isomeric mixture was prepared.

^{1}H-NMR [400 MHz, $CDCl_3$] of the octene mixture: δ [ppm] 5.46–5.35 (m, 2H), 2.02–1.94 (m, 3H), 1.64–1.63 (m, 2H), 1.39–1.24 (m, 6H), 0.903–086 (t, 3H, ${}^2J = 7.2$).

Mass spectroscopic characterization

***cis*- and *trans*-2-Octene.** MS (GC): 112 (33) [M^+], 97 (2), 84 (10), 83 (22), 82 (3), 71 (6), 70 (56), 69 (32), 68 (6), 67 (7), 65 (2), 57 (20), 56 (59), 55 (100), 54 (10), 53 (10), 52 (4), 51 (3), 50 (2).

***cis*- and *trans*-3-Octene.** MS (GC): 112 (45) [M^+], 97 (3), 84 (12), 83 (30), 82 (3), 81 (2), 79 (2), 77 (2), 71 (8), 70 (70), 69 (64), 68 (8), 67 (14), 65 (4), 57 (20), 56 (63), 55 (100), 54 (9), 53 (13), 52 (2), 51 (5), 50 (2).

***cis*- and *trans*-4-Octene.** MS (GC): 112 (34) [M^+], 97 (2), 84 (9), 83 (28), 82 (2), 81 (2), 79 (2), 77 (2), 71 (5), 70 (50), 69 (35), 68 (5), 67 (10), 66 (2), 65 (3), 57 (13), 56 (47), 55 (100), 54 (9), 53 (9), 52 (2), 51 (4), 50 (2).

Methylheptenes. MS (GC): 112 (38) [M^+], 111 (36), 97 (6), 83 (100), 81 (7), 79 (4), 78 (4), 77 (2), 76 (2), 70 (10), 68 (10), 67 (13), 65 (3), 64 (4), 63 (3), 57 (3), 56 (7), 55 (79), 54 (10), 53 (13), 52 (6), 51 (6), 50 (6).

Dimethylhexenes. MS (GC): 112 (23) [M^+], 111 (20), 84 (7), 83 (58), 82 (61), 81 (4), 80 (5), 70 (10), 69 (11), 67 (9), 66 (6), 56 (8), 54 (100), 54 (10), 53 (11), 51 (5).

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Trimers. MS (GC): 169 (1) [M^+], 168 (8), 139 (7), 123 (1), 112 (4), 111 (16), 110 (2), 109 (4), 105 (1), 98 (4), 97 (14), 96 (4), 95 (14), 93 (4), 91 (8), 85 (3), 84 (13), 83 (72), 82 (6), 80 (2), 79 (17), 77 (17), 71 (4), 70 (16), 69 (99), 68 (7), 67 (44), 66 (4), 65 (13), 63 (3), 57 (26), 56 (11), 55 (100), 54 (7), 53 (28), 52 (6), 51 (9), 50 (3).

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