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Propylene Bulk Phase Oligomerization with Bisiminepyridine Iron Catalysts: Mechanistic Investigation of 1,2- versus 2,1-Propylene Insertion[1]

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Abstract—Iron(II) complexes were synthesized with bisiminepyridine ligands of different steric demand. Activation with modified MAO (25 mol% isobutyl groups) generated very active catalysts for propylene oligomerization. These oligomerizations were carried out in liquid propylene in a heat flow calorimeter. The oligomers were separated by preparative gas chromatography and the dimers and trimers analyzed using analytical gas chromatography, ^{1}H-NMR-, and ^{13}C NMR-spectroskopy. By means of the knowledge of the dimer and trimer structure, we were able to establish a mechanistic pathway for propylene insertion and obtained knowledge about the iron alkyl species involved. Analysis of the various dimers formed allowed us to determine the percentage of 1,2- versus 2,1-propylene insertions. Considering the same iron alkyl species with ligands of different steric demand, a change in the probabilities for 1,2- versus 2,1-propylene insertions can be observed. With this knowledge, the catalyst behaviour for ligands of varying steric demand can be predicted. The question of how to produce oligomers versus polymers is one of knowing how to control the ratio of the 1.2- and 2.1-insertion. One method is to alter the steric demand in the ortho position of the ligand. The more bulky the ligand, the more often a 2,1-propylene insertion happens and, therefore, the higher the molecular mass of the oligomers, i.e., polymer is formed. Another important observation is that the formation of α-olefines is favored with a higher steric demand of the catalyst.

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There is a growing academic and industrial interest in polymerization catalysts based on bisiminepyridine complexes with iron. This type of catalysts was developed and investigated by Brookhart and co-workers and Gibson and co-workers [1, 2]. It is known that they are very active in ethylene and propylene polymerization with activation by methylaluminoxane, modified-methylaluminoxane or $Ph_3C[B(C_6F_5)_4]$, and AlR_3. Zakharov, Semikolenova, and Talsi continued with studies of ethylene polymerization over homogeneous and supported catalysts based on 2,6-bis(imino)pyridyl complexes of Fe(II) and Co(II) [3–5].

In a recent paper we described a catalytic cycle that involves an iron hydride species, which is the result of a β-H-elimination [6]. Figure 1 demonstrates the reaction schemes for the generation of active species.

Figure 2 summarizes the iron species and polymer end groups that occur with TIBA and TEA activated bisiminopyridine iron catalysts.

Figure 3 shows the influence of hydrogen on the propylene polymerization and proves with these experiments the existence of a highly active hydride species.

With the knowledge of the polymer end group formation and consideration of the experimentally proven iron hydride species, it was possible to formulate the complete catalytic reaction cycle in Fig. 4 and to upgrade the earlier published cycle from Small and Brookhart [7].

From the iron *n*-propyl species **3**, the reaction can follow two different competing courses. Through realkylation with TIBA the iron isobutyl species **1** can be generated, which continuously inserts propylene in a 2,1-step to form species **6** in propagation cycle *A*. On the other hand, 2,1-propylene insertion in species **3** in propagation cycle *B* leads to species **4**. Hence, realkylation and 2,1-propylene insertion are running in competition. After β-H-elimination from a grown polymer species **4** or **6**, the iron hydride **2** is generated and the polymers **5** and **7** are formed. The very active iron hydride **2** inserts propylene in a unique 1,2-step to form the iron *n*-propyl species **3** and the catalytic cycle is closed.

EXPERIMENTAL

All experimental procedures related to the materials, syntheses, oligomerization process, and analytical results are described in [6, 8].

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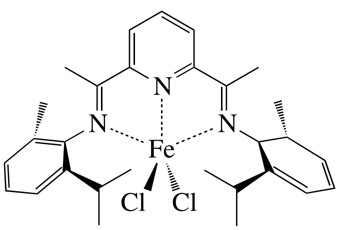
[1] The text was submitted by the authors in English.



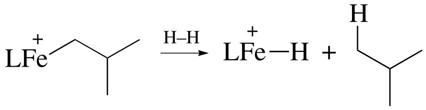
Structure of the iron complex 2,6-bis[1-(2-isopropyl-6-methylphenylimino)ethyl]-pyridineiron(II)dichloride

$$\mathrm{LFeCl_2 + (Ph_3C)[B(C_6F_5)_4] \longrightarrow Ph_3CCl + L\overset{+}{Fe}Cl\ \ B(C_6F_5)_4^-}$$

Reaction of the iron complex with borate

$$\mathrm{L\overset{+}{Fe}Cl\ \ B(C_6F_5)_4^-\ +\ Al(}\mathit{iso}\mathrm{\text{-}Bu)_3 \longrightarrow L\overset{+}{Fe}\ }\mathit{iso}\mathrm{\text{-}Bu\ {}^-B(C_6F_5)_4 + Al(}\mathit{iso}\mathrm{\text{-}Bu)_2Cl}$$

Reaction of the cationic iron species with TIBA



Reaction of the iron isobutyl species with hydrogen generating a highly active species for propylene polymerization

Fig. 1. Structure of the iron complex and reactions of the iron alkyl species.

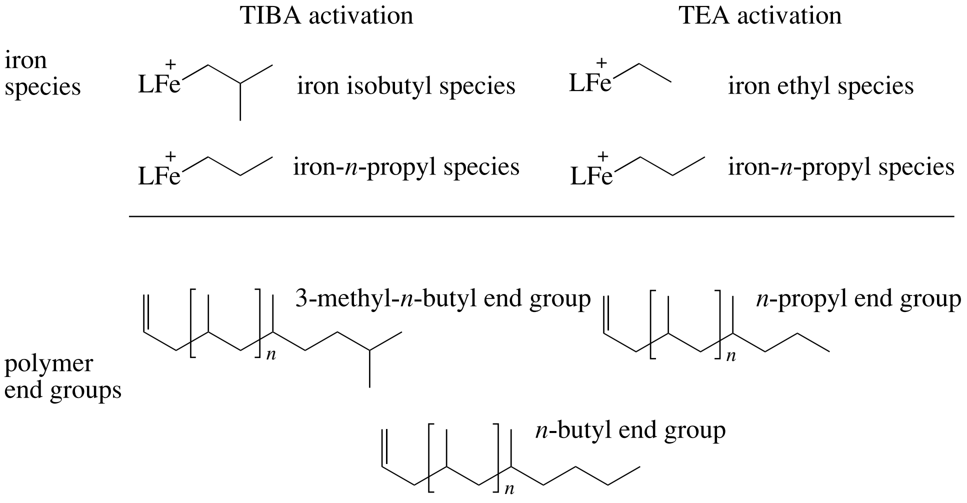


Fig. 2. Iron species and polymer end groups that occur with Al alkyl activation.

RESULTS AND DISCUSSION

To prove these catalytic cycles and to further analyze the mechanism of propylene polymerization with bisiminepyridine iron complexes, it would be ideal to isolate an iron alkyl species in order to further understand the nature of the inserting and propagating iron alkyl species. The problem is that it has not been possible to isolate such a species. Thus, we decided to regard this problem from another perspective and isolate dimers and trimers of propylene produced by different sterically demanding iron bisiminepyridine complexes. After structurally identifying the dimer or trimer it is possible to extrapolate the nature of the previous iron alkyl from which the dimer or trimer was formed.

As to the experimental procedure, we chose oligomerization in liquid propylene (bulk phase) in a heat flow reaction calorimeter (Fig. 5) in order to obtain reaction calorimeter kinetics (propene oligomerization rates as a function of different parameters) and as presenting a particular advantage for obtaining consider-

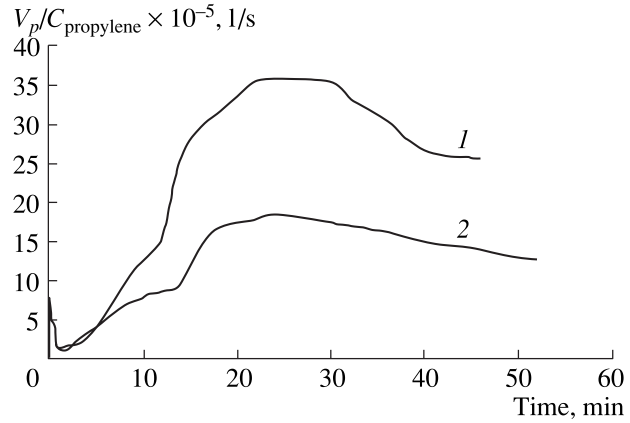


Fig. 3. Propylene polymerization rates in toluene versus time with hydrogen (*1*) and without hydrogen (*2*). [Fe] = 2.1×10^{-5} mol, $Ph_3C[B(C_6F_5)_4]$ = 2.05×10^{-5} mol, $P_{C_3H_6}$ = 1.9 bar. 0.1 ml TIBA, T_p = 16°C, solvent: toluene.

ably higher amounts of propylene dimers and trimers available for GC and MS analysis.

Figure 6 now shows the reaction calorimeter kinetics. The catalysts synthesized and investigated in this work are indicated in the boxes. The curves represent the oligomerization rates versus time at various temperatures. In general, all oligomerization rates rise strongly with increasing temperature, but after passing through a maximum they decrease strongly again. These characteristic courses are the more distinct the higher the reaction temperature is. This means that both the oligomerization reaction and a termination reaction clearly depend on the temperature. This termination reaction is obviously a side reaction of the chosen Al-alkyl with the ligand of the iron compound which leads to the destruction of the active center [9]. Further, from the maxima of the curves at the different temperatures it was possible to estimate via Arrhenius the activation energies E_a. They are in the expected range for a catalytic reaction.

Once the dimers and trimers have been correctly identified, it is possible to proceed with the mechanistic considerations. Figure 7 shows the isomer distribution of the C_6-fraction at three different temperatures produced with catalyst **1**. With increasing temperature, there is an increase in the percentage of dimer **1** (4-methyl-1-pentene) while the amount of dimer **4** (*E*-4-methyl-2-pentene) is decreased. On the other hand, the percentage of dimer **3** (Z-4-methyl-2-pen-

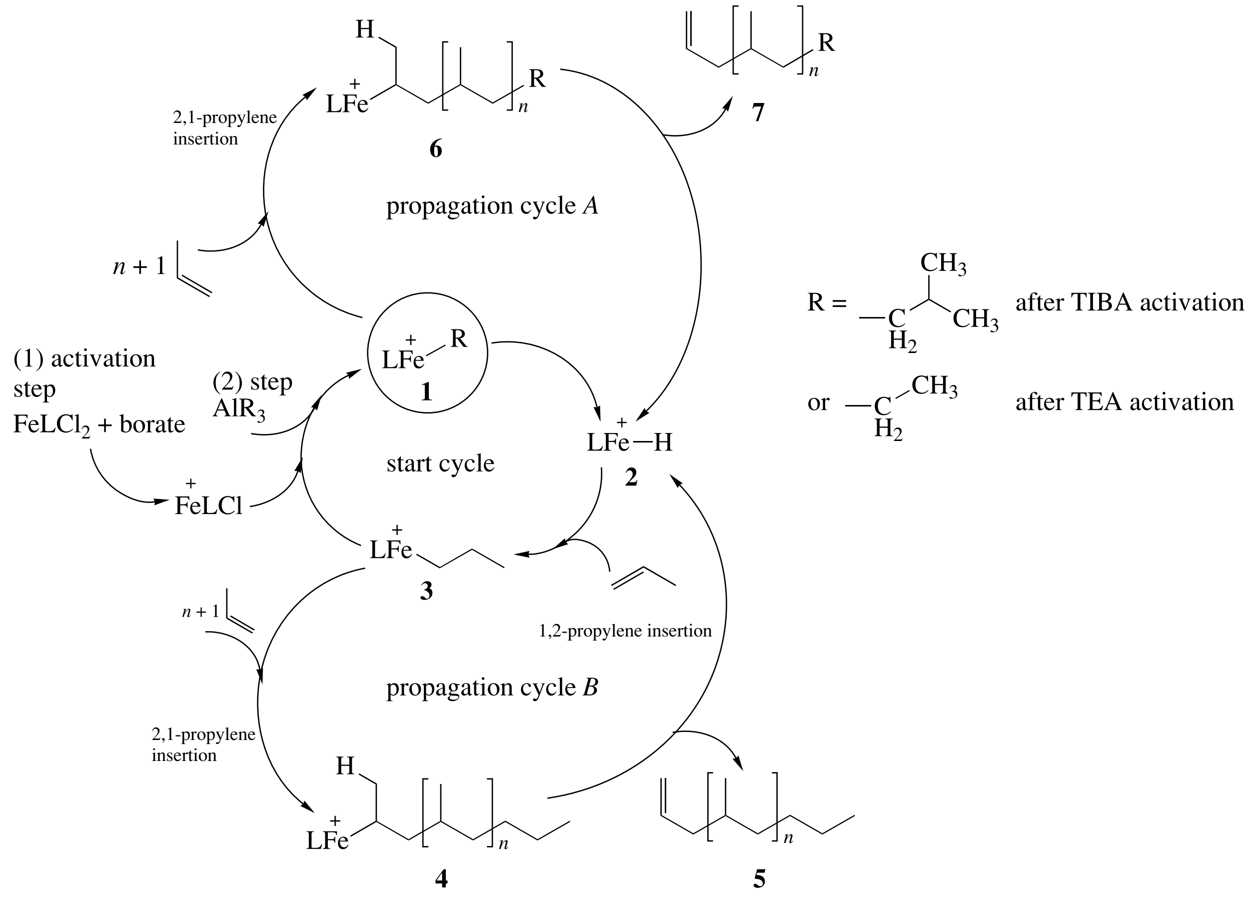


Fig. 4. Catalytic cycle for propene polymerization with bisiminepyridine iron complexes.

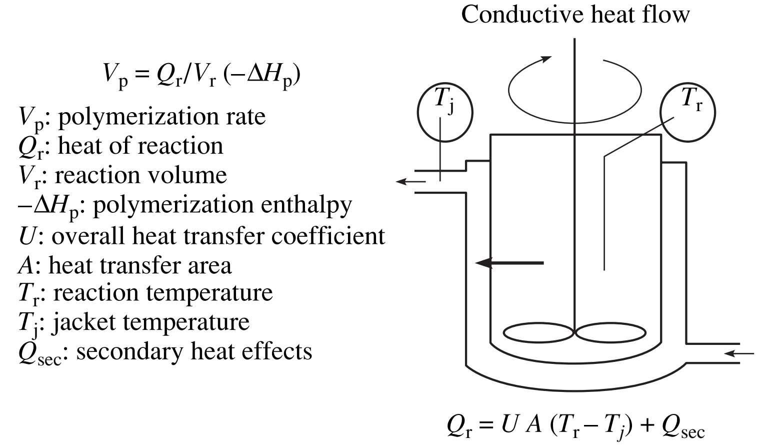


Fig. 5. Method of heat flow calorimetry for reactions in liquid propylene.

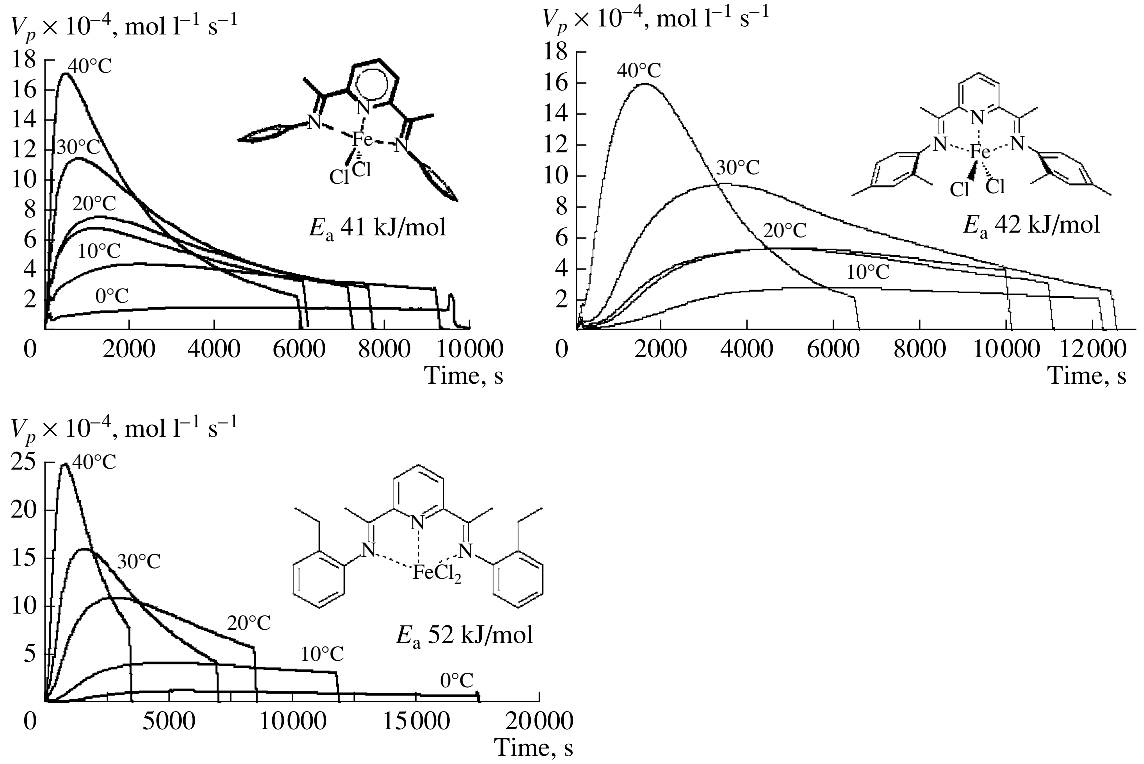


Fig. 6. Propylene oligomerization rates versus time for three catalysts of different steric demand.

tene) increases only slightly. The increasing temperature favors the formation of the 1-olefin and the *Z*-isomer of the 2-olefin.

Figure 8 illustrates all the olefins and corresponding iron alkyls that occur in this reaction. The percentage near the arrows indicates whether it is a 1,2- or 2,1-propylene insertion that occurs. In the middle of Fig. 8 is the starting hydride species. From this species there are two possibilities for a propylene insertion. Moving left (white arrow), the propylene inserts in a 1,2-arrangement and forms the iron-*n*-propyl species. From this species there are again two possible routes for an incoming propylene: the 1,2- or the 2,1-insertion. Analyzing the formed dimers, it is possible to conclude that there is a 50 to 50 probability for a propylene insertion via a 1,2- or a 2,1-step. A different situation is found when following the black arrow to the right of the hydride and starting with a 2,1-propylene insertion. The formed iron isopropyl species favors the subsequent 2,1-insertion by more than 90% about the 1,2-insertion. The iron alkyl formed after two 2,1-propylene insertions is the dominant species for

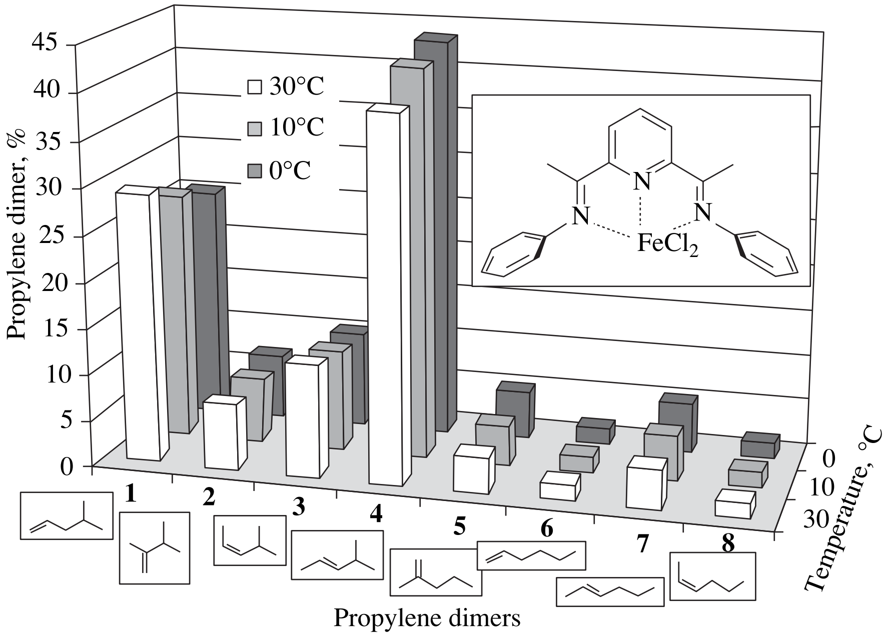


Fig. 7. Propylene isomer distribution produced with catalyst **1**. [Fe] = 4 × 10^{-5} mol/l, 1.5 ml MMAO, [Al] 3.5 × 10^{-3} mol/l, liquid propylene 99.5%, 120 min.

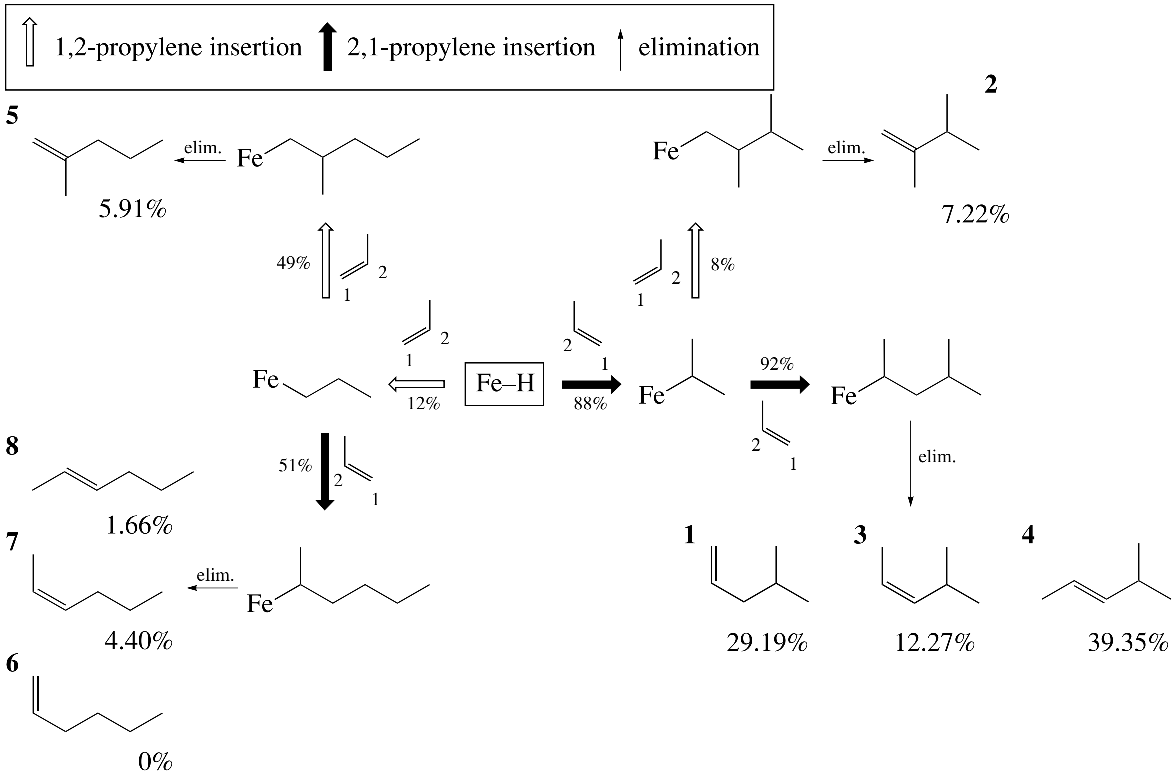


Fig. 8. Mechanistic details of propylene dimerization with catalyst **1**. For conditions see Fig. 7.

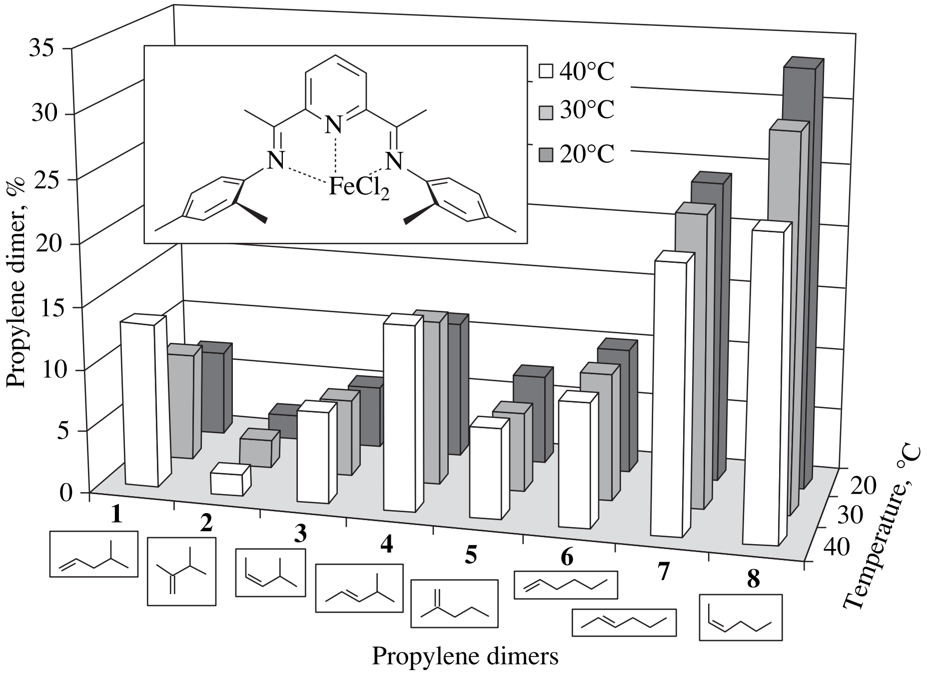


Fig. 9. Propylene isomer distribution produced with catalyst **2**. For conditions see Fig. 7.

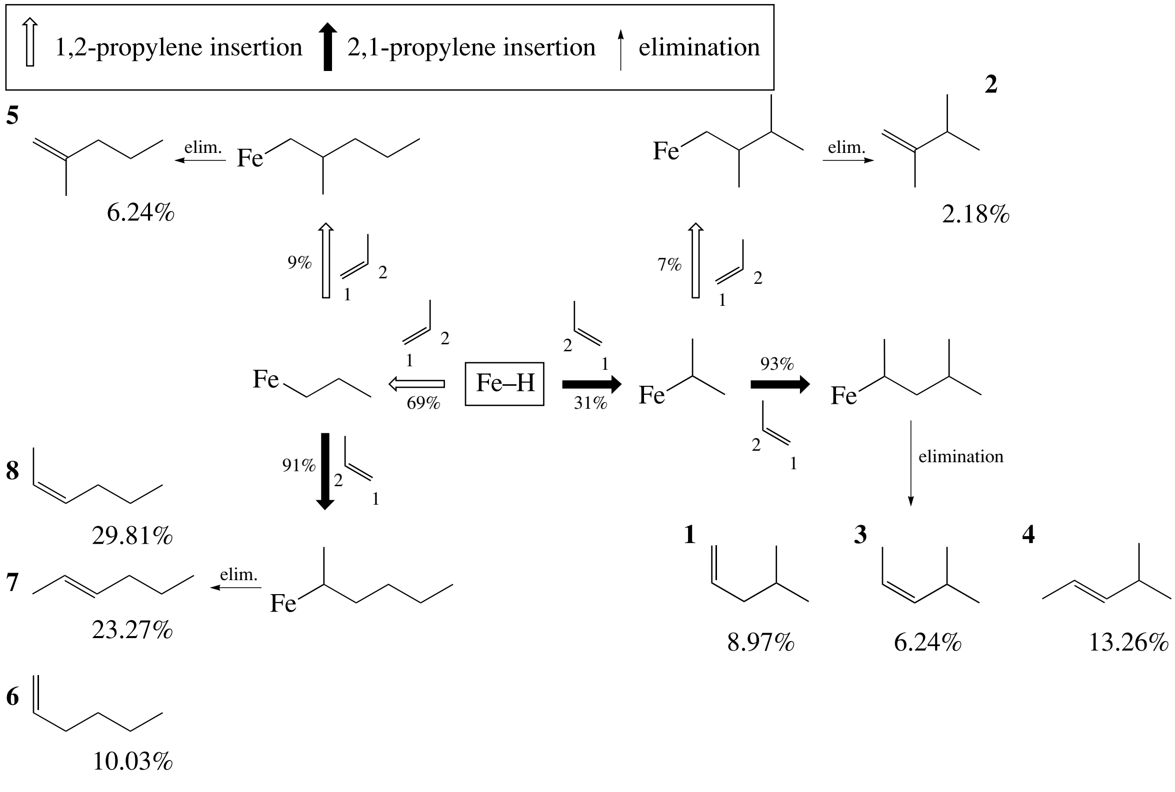


Fig. 10. Mechanistic details of propylene dimerization with catalyst **2**. For conditions see Fig. 7.

the further growth to tri- and higher oligomers. In conclusion, we can say that it is more likely that the propylene inserts in a 2,1- than in a 1,2-arrangement both in the iron hydride and the iron alkyl when we use the least sterically demanding catalyst **1**.

What happens when the steric demand of the system is increased by using catalyst **2**? Here there is a methyl group in the ortho position of the phenylimine. Figure 9 shows the distribution of the C_6-fraction produced with catalyst **2** at different temperatures.

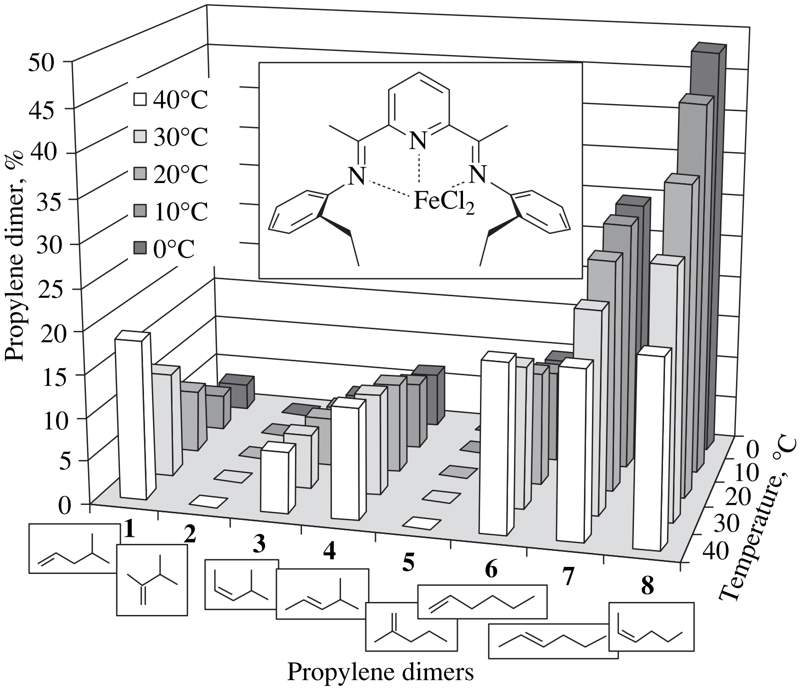


Fig. 11. Propylene isomer distribution produced with catalyst **3**. For conditions see Fig. 7.

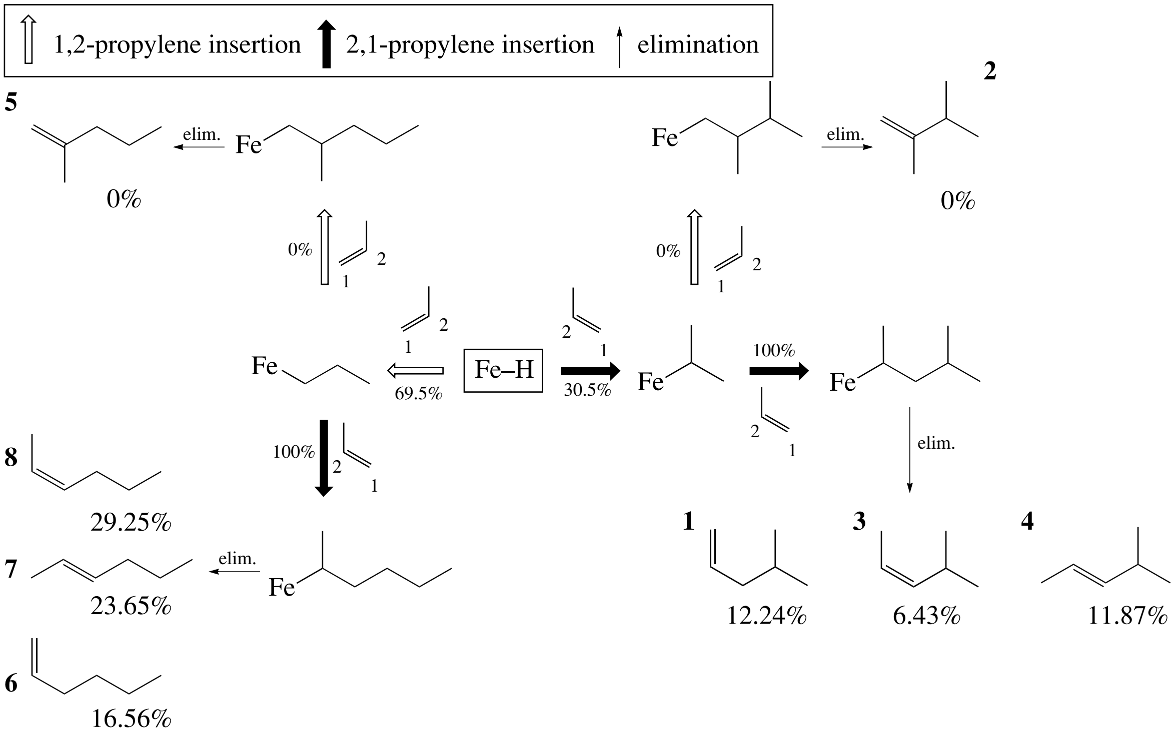
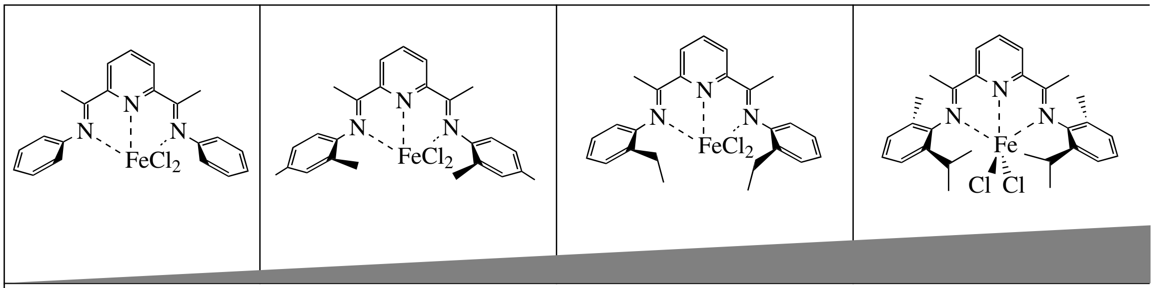


Fig. 12. Mechanistic details of propylene dimerization with catalyst **3**. For conditions see Fig. 7.



Steric demand in the ortho position of the ligand

1. Insertion in Fe–H	1,2 < 2,1	1,2 > 2,1	1,2 > 2,1	1,2 > 2,1
2. Insertion in Fe-propyl	1,2 = 2,1	2,1 > 1,2	2,1 —	2,1 —
in Fe-isopropyl	2,1 > 1,2	↓ 2,1 > 1,2	2,1 —	2,1 —

Combined sterical demand of the ligand system and the growing chain at the iron center causing the increase of the 2,1-insertion

Fig. 13. Influence of the steric demand in the ortho position of the ligand of the different iron catalysts on the decision between 1,2- versus 2,1-insertion.

This catalyst gives a completely different distribution compared to catalyst **1**. In this case, hexenes **6**, **7**, and **8** are the most populated dimers and no longer the methyl pentenes; also, increasing temperature results in an increase in the amount of the dimers **1**, **3**, and **4**. When catalyst **1** was used, there was also an increase in the dimers **1** and **3**, but a decrease in dimer **4**. This difference in the termination behaviour must relate to the slightly higher steric demand in the ligand sphere of catalyst **2**.

The mechanistic pathway for catalyst **2** is shown in Fig. 10. Comparing the behaviour of catalyst **2** and catalyst **1**, there is an interesting shift in the mechanism. The cycle begins again with the Fe–H species in the middle of Fig. 10. The higher steric demand of the ligand system leads to a 69 : 31 favored 1,2-propylene insertion (white arrow) in the iron hydride, as opposed to the 88 : 12 favored 2,1-insertion in the case of catalyst **1** Considering the second propylene insertion following the previous 2,1-insertion (black arrow), the same ratio is observed as with catalyst **1**. However, upon the second insertion after a 1,2-insertion (white arrow), there is a great change in the 2,1-insertion in the iron-*n*-propyl species: from a 51 : 49 ratio in the case of catalyst **1** to a 91 : 9 ratio in the case of catalyst **2**. It is quite interesting that the ratio is almost the same as the 93 : 7 ratio after the first 2,1-insertion. Hence, there must be a combined steric demand of the ligand system and the growing chain at the iron center, causing the increase in the percentage of 2,1-insertions. In the case of the less sterically demanding catalyst **1**, the *n*-propyl group after the first 1,2-propylene insertion can arrange itself in such a way that there is no preference for either a 1,2- or a 2,1-insertion. The two methyl groups of the iron isopropyl species have a higher steric demand than the linear *n*-propyl group, causing a more hindered center. The higher sterically demanding catalyst **2** prevents the rearrangement of the linear *n*-propyl group and the steric demand nears that of the isopropyl group.

With a higher steric demand in the ligand system, there is an increasing preference for the first 1,2-propylene insertion and an increasing tendency for the second 2,1-insertion. The next system investigated was sterically the most demanding, namely, the *ortho*-ethyl substituted catalyst **3**. Figure 11 shows the distribution of the C_6-fraction obtained with this catalyst.

Catalyst **3** follows the same general trend in dimer distribution as was observed with catalyst **1** and **2**. With the higher steric demand of the ligand system, more hexenes (**6**, **7**, and **8**) and fewer substituted pentenes (**1**, **3**, and **4**) are formed. Dimers **2** and **5** were not detected at all.

Figure 12 demonstrates the mechanistic pathway for catalyst **3**. Beginning again with the iron hydride species, almost the same probabilities for a 1,2- and a 2,1-arrangement for the initial propylene insertion are observed as with catalyst **2**. The greatest difference between the two catalysts is found in the second step. In the case of catalyst **3**, there is a 100 : 0 favored 2,1-arrangement for the second insertion, as compared with a 91 : 9 ratio using catalyst **2**.

When comparing the three catalysts, there is clearly a different behaviour. With a slightly higher steric demand in ortho position from a hydrogen to methyl, the dimer distribution dramatically changes. The change from methyl to ethyl on the ligand system does not change the distribution dramatically, but it does increase the ratio of the 1-olefins.

Considering an even more sterically demanding ligand, one would expect the first 1,2-propylene insertion into the iron hydride to be followed by several 2,1-insertions. The terminating step should result in a terminal double bond. This is exactly what is observed when a 2-methyl-6-isopropyl substituted catalyst is used [6, 7].

In Fig. 13 an attempt is finally made to systematize the influence of the steric demand in the ortho position of the catalysts ligands. The conclusion should be allowed that the second insertion seems to work as a regioselective switch that combines the steric demand of the catalysts ligands and of the growing chain on the iron center.

Our approach to the clarification of mechanisms was the isolation of oligomers and the identification of the obtained products. Knowing the exact product structure, it is possible to make reasonable approximations regarding the structure of involved iron alkyl species in the catalytic cycle without identifying the exact iron alkyl species. In this way, we were able to establish the mechanistic course for the propylene oligomerization with bisiminepyridine iron systems. The question of how to produce polymers versus oligomers is one of knowing how to control the ratio of the 1,2- and 2,1-insertions. One method is to adjust the steric demand in the ortho position of the catalyst ligand. The bulkier the ligand, the more often a 2,1-propylene insertion happens and, therefore, higher molecular masses, i.e., polymer, are formed.

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