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# Benign Catalysis with Iron: Unique Selectivity in Catalytic Isomerization Reactions of Olefins

Reiko Jennerjahn,<sup>[a]</sup> Ralf Jackstell,<sup>[a]</sup> Irene Piras,<sup>[a]</sup> Robert Franke,<sup>[b]</sup> Haijun Jiao,<sup>[a]</sup> Matthias Bauer,<sup>[c]</sup> and Matthias Beller<sup>\*[a]</sup>

The use of noble metal catalysts in homogeneous catalysis has been well established. Due to their price and limited availability, there is growing interest in the substitution of such precious metal complexes with readily available and bio-relevant catalysts. In particular, iron is a "rising star" in catalysis. Herein, we present a general and selective iron-catalyzed monoisomerization of olefins, which allows for the selective generation of

#### Introduction

The development of organometallic catalysis has been a real success story in the past decades, and the introduction of molecular-defined organometallic complexes has modernized organic synthesis and the industrial production of fine and bulk chemicals.<sup>[1]</sup> Clearly, most of the work in organometallic catalysis has been performed by applying noble metals based on palladium, rhodium, iridium, and ruthenium complexes.<sup>[2-5]</sup> Due to economic constraints, limited availability, and sometimes sensitivity and toxicity of precious metal complexes, there is growing interest in substituting such catalysts with less expensive bio-relevant metals. In this respect, homogeneous catalysis with iron complexes offers a highly attractive substitute. Hence, this area has become one of the "hot topics" in catalysis.<sup>[6-17]</sup> To date, most of the work in this field has demonstrated that iron complexes can be used in the same way as noble metal catalysts. Although this is an important goal, little is known about the development of organometallic catalysis using iron complexes. Herein, we demonstrate that a trinuclear iron carbonyl cluster in the presence of water enables a highly selective olefin isomerization reaction.

Olefin functionalization is a fundamental catalytic process that is important for organic synthesis on the laboratory scale, as well as for large-scale industrial applications.<sup>[18,19]</sup> For example, in the production of plasticizers and detergent alcohols (Shell higher olefin process), isomerization processes play a central role on the million-ton scale. Additionally, these methods are often used in the pharmaceutical and fragrance industry. In general, classic acidic and organometallic isomerization catalysts yield the thermodynamically most stable internal products. Hence, mixtures of olefins are obtained, and the selective functionalization of such mixtures continues to be a highly challenging task.<sup>[20-22]</sup> For example, in the presence of a hydrogen-activated [Rh(acac)(CO)<sub>2</sub>] (acac = acetylacetone) complex, 1-octene provides an olefin mixture consisting of 1-octene (2%), 2-octenes (11%), 3-octenes (28%), and 4-octenes (59%, 2-olefins. Typically, common metal complexes give mixtures of various internal olefins. Both bulk-scale terminal olefins and functionalized terminal olefins give the corresponding products under mild conditions in good to excellent yields. The proposed reaction mechanism was elucidated by in situ NMR studies and supported by DFT calculations and extended X-ray absorption fine structure (EXAFS) measurements.

Table 1).<sup>[20]</sup> Other precious metal complexes based on palladium or ruthenium isomerize 1-octene to similar mixtures (Table 1).<sup>[23-27]</sup> As early as 1966, Frankel et al. described the isomerization activity of simple iron pentacarbonyl complexes.<sup>[28]</sup> Again, mixtures of olefins were obtained. Further problems of known isomerization catalysts are their limited functional

lsomer	Yield [%	b]			
	Rh <sup>[a]</sup>	Pd <sup>[b]</sup>	Fe <sup>[c]</sup>	Rh <sup>[d]</sup>	$Ru^{[e]}$
$\sim\sim\sim\sim$	2	2	16	4	2
V M	11	44	36	68	37
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	28	36	33	24	43
$\sim\sim\sim\sim$	59	18	15	4	18

thalen-1-yl]-1*H*-pyrrole, 0.8 mol% *p*-toluenesulfonic acid, 1 h. [c] 5 mol% [Fe(CO)<sub>5</sub>], 1 h, 190°C. [d] 1 mol% [HRhCO(PPh<sub>3</sub>)<sub>3</sub>], 6 h, 100°C. [e] 1 mol% [H<sub>2</sub>RuCO(PPh<sub>3</sub>)<sub>3</sub>], 6 h, 100°C.

[a] Dr. R. Jennerjahn, Dr. R. Jackstell, Dr. I. Piras, Dr. H. Jiao, Prof. M. Beller Leibniz-Institut f
ür Katalyse e.V. an der Universit
ät Rostock Albert-Einstein-Stra
ße 29a, 18059 Rostock (Germany) Fax: (+ 49) 381-1281-5000 E-mail: matthias.beller@catalysis.de

- E-mail: matthias.beller
- [b] Prof. Dr. R. Franke Evonik Oxeno GmbH, 45772 Marl (Germany) and Lehrstuhl für Theoretische Chemie Ruhr-Universität Bochum, 44780 Bochum (Germany)
- [c] Dr. M. Bauer
- Fachbereich Chemie, Technische Universität Kaiserslautern Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern (Germany)
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group tolerance and the necessity to use high pressure and/or temperature. In this respect, the development of novel ruthenium complexes that perform isomerization are noteworthy.<sup>[29-34]</sup>

Based on our general interest in catalysis with iron carbonyl complexes,[35-37] we recently investigated the iron-catalyzed hydroformylation of 1-octene with synthesis gas (CO/H<sub>2</sub> = 1:1) under various conditions. Unfortunately, only low yields in aldehydes (<12%) and mixtures of octenes were obtained. To our surprise, in the absence of carbon monoxide, selective isomerization to 2-octene occurred (Figure 1). Apart from work in the early days of transition-metal catalysis, iron has been rarely investigated for catalytic isomerization processes.[38,39] Notably, Periasamy et al. described the selective conversion of aliphatic olefins in the presence of stoichiometric amounts of iron carbonyl complexes and an excess of copper salts (2 equiv) or 1,2-dibromoethane.<sup>[40]</sup> In addition, iron carbonyl complexes have been used for the isomerization of alkenols to aldehydes.<sup>[41]</sup> More recently, Harris et al. have demonstrated in detail the mechanism of photoactivating iron carbonyl complexes in the presence of alkenes.<sup>[42]</sup> Nevertheless, a general and selective iron-catalyzed olefin isomerization methodology has yet to be formulated, and the compatibility of functional groups has not yet been explored.



**Figure 1.** Selective isomerization of 1-octene in the presence of  $[Fe_3(CO)_{12}]/H_2O/KOH.$ + 1-Octene; : 2-octene; : 3-octene; : 4-octene.

#### **Results and Discussion**

We initially studied the reactivity of different iron hydride carbonyl complexes with 1-octene as the model system (Table 2). For the selective generation of hydride species through a water-gas shift reaction,[43,44] adding water and base proved to be essential. Using only iron carbonyl complexes without water and base resulted in a mixture of internal olefins (Table 2, entry 1). However, applying [Fe(CO)<sub>5</sub>], [Fe<sub>2</sub>(CO)<sub>9</sub>], or [Fe<sub>3</sub>(CO)<sub>12</sub>] in the presence of water and KOH immediately created an active isomerization species, and selective isomerization of the terminal olefin to the corresponding 2-octene took place within 1 h in > 92% yield (Table 2, entry 2). Then, for the next 5 h the composition of this mixture basically did not change. Using Collman's reagent or a combination of HCl and Collman's reagent, which is known to form the dihydride complex [H<sub>2</sub>Fe(CO)<sub>4</sub>], no activity at all was observed (Table 2, entries 7-8). However, upon standing in solution at room temperature, the monohydride complex [HFe(CO)<sub>4</sub>]<sup>-</sup> (<sup>1</sup>H NMR spec-

Table 2.         Isomerization	of	1-octene	in	the	presence	of	different	iror
complexes. <sup>[a]</sup>								

Entry	Iron source	Additive	t	Yield of octene [%] <sup>[b]</sup>			
			[h]	1-	2-	3-	4-
1 [d]			1	27.7	31	28.4	13.2
1	[1 C3(CO) <sub>12</sub> ]	-	6	16.1	36	33.1	15
2	2 [Fe (CO) ]	кон	1	4	92.8	2.8	0.4
2	[1 e <sub>3</sub> (CO) <sub>12</sub> ]	KOIT	6	1.7	92.5	5.3	0.5
<b>3</b> [c]		NaOH	1	4.2	92.7	2.8	0.3
	5 <sup>11</sup> [Fe <sub>3</sub> (CO) <sub>12</sub> ]	NaOIT	5	2.6	85.9	10.6	0.8
1 <sup>[c]</sup>		KCI	1	4.2	86.7	7.8	1.3
- T	[1 03(00)12]	KCI	6	2.8	84.4	11.3	1.6
5		кон	1	5.6	92.0	2.1	0.2
	5 [i e(CO) <sub>5</sub> ]	Kon	6	2.7	89.6	7.3	0.5
6	5 [Ee (CO) ]	кон	1	6.6	89.4	3.3	0.7
	[1 C2(CO)]	Kon	6	2.7	88.3	8.2	0.8
7 <sup>[d]</sup>	Na <sub>2</sub> [Fe(CO) <sub>4</sub> ]		6	95.1	4.8	0.1	0
8 <sup>[c]</sup>	Na <sub>2</sub> [Fe(CO) <sub>4</sub> ]	HCI	6	99.7	0.2	0.1	0
Q <sup>[d]</sup>	9 <sup>[d]</sup> Na <sub>2</sub> [Fe(CO) <sub>4</sub> ]	но	1	2.7 93.7 3	3.4	0.1	
		1120	6	2.1	77.4	18.7	1.8
10	$[Fe(BF_4)_2]$		6	99.7	0.2	0.1	0
11	[CpFe(CO) <sub>2</sub> ]		6	99.7	0.2	0.1	0
12	$Na_2[Fe(CN)_5NO]$		6	99.7	0.2	0.1	0
[a] $[Fe_3(CO)_{12}]$ (1 mol%), diglyme (2 mL), aq. KOH (0.16 mL, 3 N), 80 °C. [b] Determined by performing GC. [c] Additive used instead of KOH. [d] Without ag. KOH.							

trum,  $\delta = -8.95$  ppm) obtained by hydrolysis of Collman's reagent was slowly converted into the trinuclear anion (<sup>1</sup>H NMR spectrum,  $\delta = -14.92$  ppm),<sup>[45]</sup> which showed activity comparable with the catalyst system generated in situ (Table 2, entry 9). When the isomerization process was started with [Fe(CO)<sub>5</sub>], the same monomeric iron anion [HFe(CO)<sub>4</sub>]<sup>-</sup> was formed upon reaction with 3 equiv of NaOH or KOH. After a few hours, this species was converted to the same red-colored trinuclear anion.<sup>[43,44]</sup> When using [Fe<sub>2</sub>(CO)<sub>9</sub>] instead of [Fe(CO)<sub>5</sub>], the reaction solution turned red after 2 h. Interestingly, [Fe<sub>3</sub>(CO)<sub>12</sub>] produced the red active-catalyst solution after a few minutes. This explains the higher activity of this precatalyst relative to all the other iron carbonyl complexes. No isomerization was achieved using  $[Fe(BF_4)_2]$   $[CpFe(CO)_2]^-$  (Cp = cyclopentadienyl) and Na<sub>2</sub>[Fe(CN)<sub>5</sub>NO] (Table 2, entries 10–12). Investigations into the formation of the active catalyst with the aid of deuterium-labeling studies showed that the active iron hydride complex was formed by a classic Hieber base reaction and not by photoactivation. Hence, using a stoichiometric amount of [Fe(CO)<sub>5</sub>] in the presence of KOD and D<sub>2</sub>O led to approximately 30% deuteration of 2-octene (see the Supporting Information). This partial deuteration can be explained by the conversion of 100 mol% iron pentacarbonyl to 33 mol% of  $[DFe_3(CO)_x]^-$ . After one catalytic isomerization cycle,  $[HFe_3(CO)_x]^-$  was generated by  $\beta$ -hydride elimination from the olefin, and further deuteration did not occur.

A remarkable feature of this reaction is the selective monoisomerization process. At first glance, there is no reason why the isomerization should stop at the  $\beta$ -position. Thermodynamic control would lead to a mixture of internal olefins similar to that of entry 1 in Table 2. To investigate the nature of the selective  $\alpha$ -to- $\beta$  isomerization, we performed reactions with stereochemically pure 2-octenes and a *E/Z* mixture of 2-octene (see the Supporting Information, Table S2). The different behavior of these olefins is shown in Scheme 1. Beginning with



Scheme 1. Isomerization of Z- and E-2-octene with [Fe<sub>3</sub>(CO)<sub>12</sub>]/H<sub>2</sub>O/KOH.

pure *E*-2-octene, almost no conversion was observed. However, in the case of the *E/Z* mixture with 79% *Z*-olefin, selective conversion took place from *Z*-2-octene into *E*-2-octene. Apparently, the selectivity for the terminal olefin is based on the steric demand of the iron complex. To understand this peculiar behavior in more detail, we carried out a comprehensive DFT study into the reaction mechanism using 1-butene as the model olefin. On the basis of the observed change in reaction rate and solution color with different precatalysts in our experimental work, we assumed that the active catalyst should be triiron carbonyl clusters, [HFe<sub>3</sub>(CO)<sub>*x*</sub>]<sup>-</sup>. Nevertheless, our computational search for the catalytically active species comprised monoiron and diiron carbonyl clusters, as well as complexes such as [HFe<sub>3</sub>(CO)<sub>*x*</sub>]<sup>-</sup> with *x* = 11–8.

Unexpectedly, only in the case of  $[{\rm HFe}_3({\rm CO})_8]^-$  the free energy and enthalpy of binding of

1-butene were not positive: Figure 2 shows the calculated energy profile and selected optimized structures for the proposed reaction mechanism. The binding energy of 1-butene, 2-Zbutene, and 2-E-butene is -12.0, -10.7, and -10.5 kcalmol<sup>-1</sup>, respectively. The H-Fe insertion into the 1-butene double bond starting from HFe(1-butene) via TS1 corresponds to a barrier of 10.6 kcal mol<sup>-1</sup>. Our hitherto conducted calculations of intermediate and transition-state-like structures indicate that the reorientation in the Fe(2-butyl)-1 complex towards the Fe(2butyl)-2 complex proceeded via two adjacent transition states. This type of pathway is known as a two-step no-intermediate mechanism and has been reported for isomerization reactions amongst others.<sup>[46]</sup> The barrier Fe(2-butyl)-2 between and butene adducts HFe(2-E-butene) and HFe(2-Z-butene) is 5.8 and

5.4 kcalmol<sup>-1</sup>, respectively. Dissociation of these adducts gave the 2-butene species and the active catalytic complex [HFe<sub>3</sub>(CO)<sub>8</sub>]<sup>-</sup>. Both Fe(2-butyl)-1 and Fe(2-butyl)-2 have a triply bridging CO ligand over three metal centers and a terminal CO ligand on the face site of the three iron centers. Based on the exploration of the energy hypersurface in the neighborhood of these stationary points, we presume that these specific geometric configurations cause rotation of both H and CH<sub>3</sub> groups without significant steric hindrance. For alkyl groups larger than CH<sub>3</sub> (olefins with a double bond located more internally than position 2), however, this steric hindrance becomes significant and suppresses the rotation of these alkyl groups. The observed selectivity was determined by using the 2-butyl rotation between Fe(2-butyl)-1 and Fe(2-butyl)-2. Because the rotation of 2-butyl in TS5 needs a higher barrier than in TS4, the transformation from Fe(2-butyl)-1 to Fe(2-butyl)-2 is easier than the back transformation. As for the equilibrium between Fe(2-butyl)-1 and Fe(2-butyl)-2, the expected isomer ratio based on calculations should be about 91% for 2-E-butene and 9% for 1-butene. This computed isomer ratio agrees reasonably well with the observed isomer distribution (Table 2, entry 1).

In summary, the proposed isomerization mechanism starts from the 1-alkene complex and forms either 2-*E*-alkene or 2-*Z*-alkene. The important step is the formation of Fe(2-butyl)-1 with a CH agostic interaction after H–Fe insertion. Because the iron center contains only one free coordination site, the



Figure 2. Energy profiles (associated optimized structures are shown in the Supporting Information).

coordinated alkyl group has to rotate for isomerization. The decisive factor is the detachment of the C-H agostic interaction with subsequent rotation over the sterically demanding triply bridged CO. This rotation is the governing force for 2-alkene selectivity: a small CH<sub>3</sub> group can rotate in one direction [Fe(2butyl)-1 to TS4], whereas the rotation of a group larger than CH<sub>3</sub> is more hindered by the triply bridging CO ligand [Fe(2-butyl)-2 to TS5].

Table 3. Results of fitting of experimental EXAFS data with theoretical models.									
Sample	Abs-Bs <sup>[a]</sup>	<i>N</i> (Bs) <sup>[b]</sup>	<i>R</i> (Abs–Bs) <sup>[c]</sup> [Å]	$\sigma$ (Abs–Bs) <sup>[d]</sup> [Å <sup>-1</sup> ]	E <sub>f</sub> <sup>[e]</sup> [eV]	$Fl \times 10^{4[f]}$			
[Fe <sub>3</sub> (CO) <sub>12</sub> ] (solid)	Fe–C	4.7 <sup>[g]</sup>	1.81±0.02	$0.063 \pm 0.006$	6.86	3.3			
	Fe—Fe	2 <sup>[g]</sup>	$2.56\pm0.02$	$0.089 \pm 0.018$	14.51	11.1			
[Fe <sub>3</sub> (CO) <sub>12</sub> ] (1 mol %) <sup>[h]</sup>	Fe–C	$4.9\pm0.5$	$1.78 \pm 0.02$	$0.050\pm0.005$	9.48	4.9			
	Fe—Fe	$1.8\pm0.4$	$2.53\pm0.02$	$0.077 \pm 0.015$	15.98	8.0			
[Fe <sub>3</sub> (CO) <sub>12</sub> ] (1 mol%)	Fe–C	$5.0\pm0.5$	$1.79\pm0.02$	$0.055\pm0.006$	6.97	6.6			
and 1-octene <sup>(i)</sup>	Fe—Fe	$1.7\pm0.3$	$2.52\pm0.02$	$0.074 \pm 0.015$	16.78	7.5			

[a] Abs = X-ray absorbing atom, Bs = backscattering atom. [b] Number of backscattering atoms. [c] Abs—Bs distance. [d] Debye–Waller-like factor. [e] Fermi energy to account for phase shift between experiment and theory. [f] Quality of fit represented by the fit index (FI). [g] Value fixed to the crystallographic number. [h] In diglyme/KOH at RT. [i] In diglyme/KOH at 80 °C.

Then, extended X-ray absorption fine structure (EXAFS) studies were performed to prove the existence of a trinuclear iron cluster in solution. The obtained spectra for the pre-catalyst [Fe<sub>3</sub>(CO)<sub>12</sub>], and the progress of its reaction within 30 min in diglyme/KOH at room temperature are presented in the Supporting Information (Figure S2). Fe–C and Fe–Fe distances obtained for [Fe<sub>3</sub>(CO)<sub>12</sub>] agree well with the literature,<sup>[47]</sup> although a weighting of Fe–C contribution to the shorter distances was again observed.<sup>[48]</sup> stable calculated complexes HFe(1-butene) and HFe(2-*E*-butene). Notably, no fragmentation of the Fe<sub>3</sub> cluster is observed because the Fe–Fe coordination number remains at two within the error bar. Within the framework of X-ray absorption experiments, mono- and diiron clusters could therefore also be excluded as catalysts.

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Finally, we investigated the scope of this unusual mono-isomerization process. As shown in Table 4, various  $\alpha$ -olefins are transformed highly selectively to the corresponding  $\beta$ -olefins.

In the diglyme/KOH solution, the Fe--C, coordination number is slightly higher than in the [HFe<sub>3</sub>CO<sub>8</sub>]<sup>-</sup> complex of the calculations (Table 3), but changes in the electronic structure are indicated by the reduced Fe--C and Fe-Fe bond distances and X-ray absorption near edge structure (XANES) spectra (see the Supporting Information, Figure S3), in which it is apparent that the shape is modified. Oxidationstate changes hardly affect the edge position,[49] but the resonance shift at about 7.13 keV is in accordance with the formation of a negatively charged carbonyl cluster.<sup>[49]</sup> The so-called pre-edge signal at the lowenergy side of the edge at around 7.12 keV shows two signals for [Fe<sub>3</sub>(CO)<sub>12</sub>], which is a result of the nonequivalent iron centers. In solution, only one shoulder can be found, and equivalent iron centers are assumed. The Fe-Fe coordination number is proof of the intact Fe<sub>3</sub> cluster core. In the course of isomerization of 1-octene, the Fe--C coordination number of five is in good agreement with the most

Table 4. Iron-catalyzed isomerization: scope and limitations.<sup>[a]</sup> Entry Substrate Yield<sup>[b]</sup> Product E/Z Conv. Т t [%]<sup>[b]</sup> [°C] [h] [%] 20 4 5 6 400 51 20 49 3.2 1 96 80 1 93 3.1 2<sup>[c]</sup> 97 CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>CH<sub>2</sub> 100 6 96 CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>CH<sub>2</sub> 2.9 3<sup>[c,d]</sup> 97 97 100 1 3.0 4<sup>[c]</sup> 81 87 100 6 4.9 5<sup>[c,d]</sup> 93 100 6 90 6.1 6<sup>[c]</sup> 92 100 6 77 2.4 7<sup>[c]</sup> 22 97 97 100 8 >99 80 6 >99 18.9 >99 80 6 >99 15.4 9 88<sup>[e]</sup> 100 6 88 4.2 94<sup>[e]</sup> 22 94 100 4.4 2.3 10 >99 80 6 > 99 3.6 >99 80 6 >99 99<sup>[e]</sup> 11 100 6 99 3.8 99<sup>[e]</sup> 22 3.9 100 99 12 98 80 20 98 2.0 66 100 6 3.8 66 13<sup>[f]</sup> >99 100 22 >99 3.4

[a] Reactions were carried out at 80  $^{\circ}$ C with [Fe<sub>3</sub>(CO)<sub>12</sub>] (1 mol%), diglyme (2 mL), aq. KOH (0.16 mL, 3 N), and substrate (5 mmol). [b] Determined by performing GC. [c] Reaction temperature was 100  $^{\circ}$ C and 2.5 mmol of substrate was used. [d] THF was used as solvent. [e] KCl used instead of KOH. [f] Yield and selectivity determined by performing NMR spectroscopy.

Most notably, functional groups such as halides, hydroxyl, and amines are tolerated by the iron catalyst (Table 4, entries 3, 4, 10, and 12). In a number of cases, unprecedented isomerization reactions take place. For example, the generation of 2butene-1-ol from 3-butene-1-ol is remarkable (Table 4, entry 4). To the best of our knowledge, all known isomerization methods for this substrate led to butyraldehyde, which is the thermodynamically stable product of further isomerization and subsequent tautomerization reactions. Similarly, *N*-benzyl-*N*-3butenylamine (Table 4, entry 6) leads to the corresponding enamine, which undergoes uncatalyzed tautomerization towards the imine (Table 4, entry 5). 2-Vinylcyclohexane also gave the less stable exocyclic olefin in excellent yield (97%; Table 4, entry 7). Typically, using this type of substrates isomerization to endocyclic olefins is achieved.

From a practical point of view, the licorice-fragrance anethole was easily available from the isomerization reaction of estragole in >99% yield (Table 4, entry 9). In this case, the reaction exclusively with [Fe(CO)<sub>5</sub>] gave an *E/Z* ratio of 6.7 at 140 °C after 8 h.<sup>[50]</sup> Applying our system under milder conditions (80 °C), we obtained full conversion after 1 h and observed a significantly improved *E/Z* ratio of 15.4 after 6 h. Likewise, the isomerization of allyl benzene gave  $\beta$ -methylstyrene in excellent yield (>99%) with high *E/Z* selectivity (Table 4, entry 8). Using renewable products, such as citronellene, demonstrated that it was possible to selectively shift a terminal double bond in the presence of internal double bonds (Table 4, entry 12). Even more complex natural compounds such as quinine were transformed into the corresponding  $\beta$ -olefins (Table 4, entry 13).

#### Conclusions

We describe a general and selective iron-catalyzed isomerization of terminal olefins. In the presence of inexpensive and easily available iron carbonyl complexes and water, an unusual triironhydride carbonyl cluster with only eight CO ligands is formed as the active species. Unprecedented isomerization reactions of terminal olefins take place under mild conditions. Starting with industrially available terminal olefins, interesting olefin building blocks can be synthesized smoothly and with improved efficiency relative to previously known procedures.

At this point, it should be noted that successful conversion is also possible in the presence of KCl instead of KOH (Table 4, entries 9 and 11). This modification of our procedure should be sensible when base-sensitive substrates have to be used. The lower activity of the catalyst system is explained by a decreased tendency to generate the iron hydride by a water-gas shift reaction.

#### **Experimental Section**

General procedure: A Schlenk tube was charged with  $[Fe_3(CO)_{12}]$  (51 µmol, 25.7 mg), diglyme (2 mL), and a solution of KOH in H<sub>2</sub>O (0.16 mL, 3 N) under argon. After generating the catalyst in situ by stirring, 1-octene (5.1 mmol, 0.8 mL) was added and heated to 80–100 °C. The reaction was monitored by performing GC. Reactions

involving volatile compounds were carried out in an autoclave. Product characterization was performed by comparing their <sup>1</sup>H and <sup>13</sup>C NMR and HR–MS spectra to those of authentic samples,.

As an example, 1-hexadecene (2.5 mmol, 730 µl) was used following the general procedure. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 5.42–5.38 (2H, m), 2.03–1.91 (2H, m), 1.64–1.57 (3H, m), 1.25 (22H, br. s), 0.89–0.85 ppm (3H, m); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 131.7 (0.75 CH), 130.9 (0.25 CH), 124.5 (0.75 CH), 123.6 (0.25 CH), 32.6 (CH<sub>2</sub>), 32 (CH<sub>2</sub>), 29.7–29.3 (9 CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 18 (CH<sub>3</sub>), 14.1 ppm (CH<sub>3</sub>); MS (70 eV, El): *m/z* (%): 224 ([*M*]<sup>+</sup>, 41.10), 111 (45.07), 97 (82.35), 83 (80.15), 69 (81.61), 55 (100.00), 43 (55.00), 41 (57.40), 29 (18.29); HR-MS (El): *m/z* calcd for C<sub>16</sub>H<sub>32</sub>: 224.24985 [*M*]<sup>+</sup>; found: 224.249942.

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Please note: Minor changes have been made to this manuscript since its publication on *ChemSusChem's* Early View page. Specifically, Ref. [38b] was added after it was by mistake omitted from the manuscript's production data. The Editor and authors apologize for any inconvenience caused.

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