

# Isomerization of olefins by titanocene and zirconocene alkyne complexes

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## Abstract

An efficient isomerization of aliphatic and cyclic olefins is achieved by using well-defined metallocene alkyne complexes as catalysts. Titanocene complexes isomerize 1-alkenes to internal alkenes under mild conditions. The titanium complex was recovered quantitatively. Cyclic olefins, e.g. cyclohexadienes, also undergo isomerization, but a competing intermolecular hydrogen transfer reaction takes place as well. This side-reaction is much more favoured for zirconocene than for titanocene complexes.

**Keywords:** Isomerization; Aliphatic olefins; Cyclic olefins; Intermolecular hydrogen transfer; Titanocene; Zirconocene; Alkyne complexes

## 1. Introduction

The isomerization of functionalized substrates plays an important role in a great number of transition metal catalyzed reactions. Among these the olefin isomerization has the widest application.

The transition metal catalyzed isomerization of terminal olefins to internal olefins has been extensively studied [1]. In this context the catalytic activity of the low-valent titanocene species has been previously described (e.g. hydrogenation [2], isomerization [3], polymerization [4]), whereat 'Cp<sub>2</sub>Ti' was prepared in situ by reaction of Cp<sub>2</sub>TiCl<sub>2</sub> with various reducing agents (e.g. Mg, RMgX, RNa, LiAlH<sub>4</sub>) [5].

Several mechanisms for the transition metal catalyzed isomerization of alkenes are plausible.

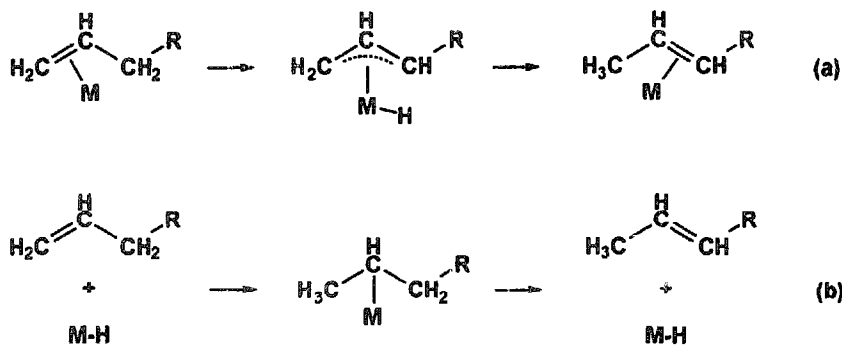
The two generally established though fundamentally different reaction pathways are the  $\pi$ -allyl metal hydride mechanism (Scheme 1, a) and the metal hydride addition–elimination mechanism (Scheme 1, b).

The  $\pi$ -allyl metal hydride mechanism (a) implies a metal induced intramolecular 1,3-hydrogen shift via an  $\eta^3$ -allyl hydride species, whereas the metal hydride addition–elimination mechanism (b) involves  $\beta$ -hydrogen elimination from a secondary metal alkyl. Thus, mechanism b is an intermolecular process, requiring a stable metal hydride species as a catalyst.

We present here our results for the isomerization of aliphatic and cyclic olefins and diolefins using several titanocene ([Cp<sub>2</sub>Ti(Me<sub>3</sub>SiC≡CSiMe<sub>3</sub>)] [6], [Cp<sub>2</sub>Ti(Me<sub>3</sub>SiC≡C<sup>t</sup>Bu)] [7], [Cp<sub>2</sub>Ti(Me<sub>3</sub>SiC≡CPh)] [8]) and zirconocene alkyne complexes ([Cp<sub>2</sub>Zr(thf)(Me<sub>3</sub>SiC≡CSiMe<sub>3</sub>)] [9],

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Scheme 1. Different mechanisms for the isomerization of olefins: (a)  $\pi$ -allyl metal hydride mechanism, (b) metal hydride addition–elimination mechanism.

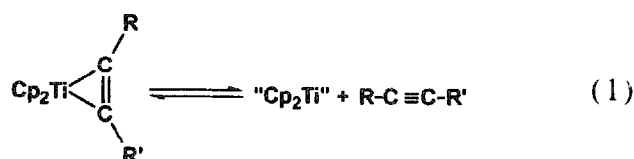
[ $\text{Cp}_2\text{Zr}(\text{py})(\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3)$ ] [10]) as precatalysts, which generate titanocene or zirconocene as the catalytic active species. The isomerizations are true catalytic reactions, yielding the precatalyst complex nearly quantitatively unchanged. This paper describes the method used for the isomerization of alkenes and dienes under mild conditions.

## 2. Results and discussion

Metallocene alkyne complexes are highly reactive towards unsaturated substrates (e.g. ketones, acetylene dicarboxylates, diynes [11]), but little is known about their catalytic activity. For this reason we investigated the isomerization of olefinic double bonds by catalytic amounts of titanocene and zirconocene alkyne complexes in regard to their activity and selectivity.

We found that metallocene alkyne complexes can, in fact, isomerize olefins under mild conditions, whereas obvious differences in the activity of the various complexes appeared: zirconocene complexes are mainly inactive in isomerization reactions of aliphatic alkenes and dienes; while the activity of the titanocene complexes is dependent on the nature of the alkyne ligand. A decreasing catalytic activity of the alkyne complexes in the sequence [ $\text{Cp}_2\text{Ti}(\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3)$ ] > [ $\text{Cp}_2\text{Ti}(\text{Me}_3\text{SiC}\equiv\text{C}^t\text{Bu})$ ] > [ $\text{Cp}_2\text{Ti}(\text{Me}_3\text{SiC}\equiv\text{CPh})$ ] was established. This corresponds on one hand to the different strengths of alkyne complexation influencing the equilibrium between coord-

inated and free titanocene (Eq. 1) and on the other hand to the tendency of used alkynes to allow coupling reactions [7,11].



The unique and really surprising feature of these complexes with sterically overcrowded silylalkynes is the tendency to form the free 'Cp<sub>2</sub>Ti' unit and to prevent coupling reactions of the alkyne [7,11]. The formation and amount of 'Cp<sub>2</sub>Ti' as the active species in the catalytic reaction is therefore dependent on the stability of the metallocene complexes.

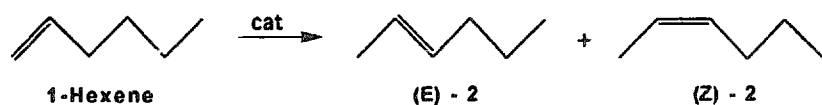
Table 1 and Table 2 summarize the results of the isomerization of aliphatic olefins.

All experiments were conducted in neat olefin without an additional solvent, using a 1:50 catalyst/substrate ratio. At the end of the reaction the alkyne complexes were nearly quantitatively recovered.

These isomerizations are exclusive transformations of 1-olefins to 2-olefins producing preferentially the *E*-isomers. This is in accordance with the factors influencing the thermodynamic stability of olefins:

1. the stability increases with the number of alkyl groups at the C–C double bond;
2. the *trans*-conformation of an olefin is more stable than the *cis*-conformation;
3. in general conjugated olefins are more stable than the isomers with isolated double bonds (except for cyclic olefins).

Table 1  
Isomerization of 1-hexene



Catalyst (cat:sub = 1:50)	<i>T/t</i> °C/h	Conversion [%]	Products [%]	
			( <i>E</i> )-2	( <i>Z</i> )-2
[Cp <sub>2</sub> Ti(Me <sub>3</sub> SiC≡CSiMe <sub>3</sub> )]	25/1	50	87.5	12.5
	25/3	97	88.9	11.1
	25/24	99	88.5	11.5
[Cp <sub>2</sub> Ti(Me <sub>3</sub> SiC≡C <sup>t</sup> Bu)]	25/3	91	83.3	16.7
[Cp <sub>2</sub> Ti(Me <sub>3</sub> SiC≡CPh)]	25/3	16	87.5	12.5
[Cp <sub>2</sub> Zr(thf)(Me <sub>3</sub> SiC≡CSiMe <sub>3</sub> )]	25 <sup>a</sup> /3	0	–	–

<sup>a</sup> Same result at 60°C.

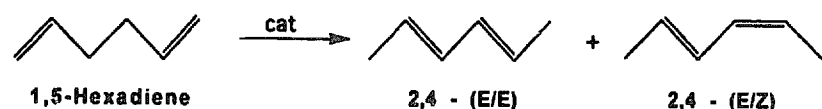
In accord with these considerations the standard heat of formation ( $\Delta H_f$ , 298 K) decreases with increasing stability in the sequence 1-hexene ( $-41.7 \text{ kJ mol}^{-1}$ ), *cis*-2-hexene ( $-48.4 \text{ kJ mol}^{-1}$ ), and *trans*-2-hexene ( $-52.5 \text{ kJ mol}^{-1}$ ) [12].

Because <sup>1</sup>H NMR experiments were unsuccessful to establish the mechanism the  $\pi$ -allyl metal hydride mechanism (a) (Scheme 1) was

assumed, which was accepted also for comparable systems [5].

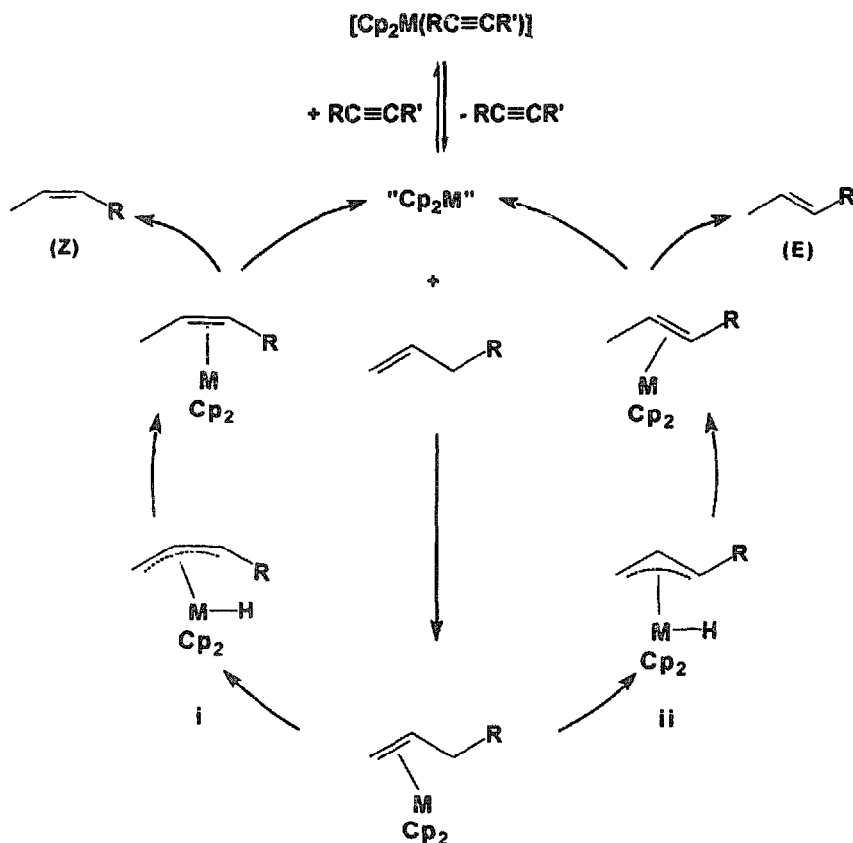
Following the dissociation of the alkyne ligand the olefin can coordinate to the generated 'Cp<sub>2</sub>M' fragment (Scheme 2). The oxidative addition of an allylic C–H bond to the metal leads to the formation of a  $\pi$ -allyl metal hydride complex for which the conformations **i** and **ii** are possible. Energetically preferred is apparently the  $\eta^3$ -allyl

Table 2  
Isomerization of 1,5-hexadiene



Catalyst (cat:sub = 1:50)	<i>T/t</i> °C/h	Conversion [%]	Products [%]	
			2,4-( <i>E/E</i> )	2,4-( <i>E/Z</i> )
[Cp <sub>2</sub> Ti(Me <sub>3</sub> SiC≡CSiMe <sub>3</sub> )]	25/1	47	85.7	14.3
	25/3	92	85.3	14.7
	25/24	96	84.7	15.3
[Cp <sub>2</sub> Ti(Me <sub>3</sub> SiC≡C <sup>t</sup> Bu)]	25/3	82	85.1	14.9
[Cp <sub>2</sub> Ti(Me <sub>3</sub> SiC≡CPh)]	25/3	17	83.9	16.1
[Cp <sub>2</sub> Zr(thf)(Me <sub>3</sub> SiC≡CSiMe <sub>3</sub> )]	25 <sup>a</sup> /3	0	–	–
[Cp <sub>2</sub> Zr(py)(Me <sub>3</sub> SiC≡CSiMe <sub>3</sub> )]	25 <sup>a</sup> /3	0	–	–

<sup>a</sup> Same result at 60°C.



Scheme 2. Proposed  $\pi$ -allyl mechanism for the isomerization of aliphatic olefins by metallocene alkyne complexes.

intermediate **ii** with the substituent R at C3 in *syn*-position to the hydrogen at C2. This is in accordance with the *E*-isomer being the main product.

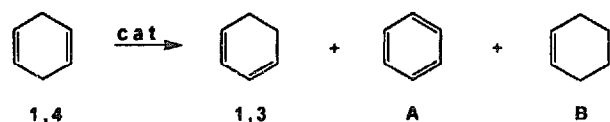
Interestingly, aliphatic olefins are exclusively isomerized by transforming a primary to a secondary double bond yielding the thermodynamically preferred product. Thus 1-hexene is isomerized to a mixture of (*E*)- and (*Z*)-2-hexene but the latter is neither isomerized to 1- or 3-hexene nor is the established ratio of *cis:trans* hexene changed. This is shown by the results obtained by using one catalyst and different reaction time (table 1 and 2), giving a *cis*- to *trans*-ratio independent of time. So, the isomerizations of 1-hexene by  $[\text{Cp}_2\text{Ti}(\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$  yields nearly the same (*E*):(*Z*) ratio ( $\approx 88:12$ ) after 1 and 3 h as well as after 24 h. The same findings were obtained in the isomerizations of 1,5-hexadiene by  $[\text{Cp}_2\text{Ti}(\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ . Only the percentage turnover is time dependent whereas the 2,4-(*E/E*):2,4-(*E/Z*) ratio of the

product ( $\approx 85:15$ ) is not changed with prolonged reaction time.

Also cyclic alkenes, e.g. 1,3- and 1,4-cyclohexadienes, were used as substrates in the isomerization. This reaction were conducted previously with other transition metal catalysts too [13]. Table 3 and Table 4 summarize our results of the isomerizations of cyclic diolefins. At room temperature only little or no isomerization is observed. The reactivity increases with the temperature, but at 60°C two competitive reactions occur, the isomerization as well as a hydrogen transfer reaction yielding benzene and cyclohexene.

The data given in Table 3 and Table 4 show for the reactions at 60°C that a large amount of the cyclohexadiene is transformed into cyclohexene and benzene, but 1,4-cyclohexadiene is disproportionated more slowly and beside this hydrogen transfer a considerable isomerization to the corresponding 1,3-diene (up to 52%) takes place.

Table 3  
Isomerization of 1,4-cyclohexadiene



Catalyst	T/t	Conversion	Product distribution [%]			
			1,3	A	B	1,4
(cat:sub = 1:50)	°C/h	[%]				
[Cp <sub>2</sub> Ti(Me <sub>3</sub> SiC≡CSiMe <sub>3</sub> )]	25/3	15	14.0	–	–	85
	60/3	78	44.0	16.5	17.0	22
	60/24	85	33.0	26.0	25.5	15
[Cp <sub>2</sub> Ti(Me <sub>3</sub> SiC≡C <sup>t</sup> Bu)]	60/3	75	52.0	11.5	11.0	25
[Cp <sub>2</sub> Ti(Me <sub>3</sub> SiC≡CPh)]	60/3	100	–	52.5	44.5 <sup>a</sup>	0
[Cp <sub>2</sub> Zr(thf)(Me <sub>3</sub> SiC≡CSiMe <sub>3</sub> )]	60/3	36	2.5	19.0	13.5	64
[Cp <sub>2</sub> Zr(py)(Me <sub>3</sub> SiC≡CSiMe <sub>3</sub> )]	60/3	30	2.5	16.5	10.5	70

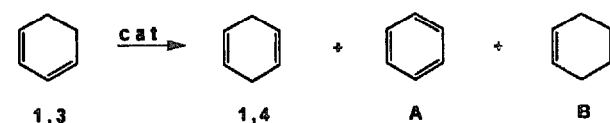
<sup>a</sup> 2.5% cyclohexane.

In contrast to the isomerization of aliphatic olefins the isomerization of cyclohexadienes seems to be in principle reversible, because 1,4-cyclohexadiene is of nearly the same stability compared to the corresponding 1,3-isomer (the conjugated isomer having a free-energy stabilization over the 1,4-compound of only 2.4 kJ mol<sup>-1</sup> [14]). This is a specific feature of cyclohexadienes, since in

acyclic systems or larger cycles the conjugated isomer is more stable than the unconjugated isomer [14].

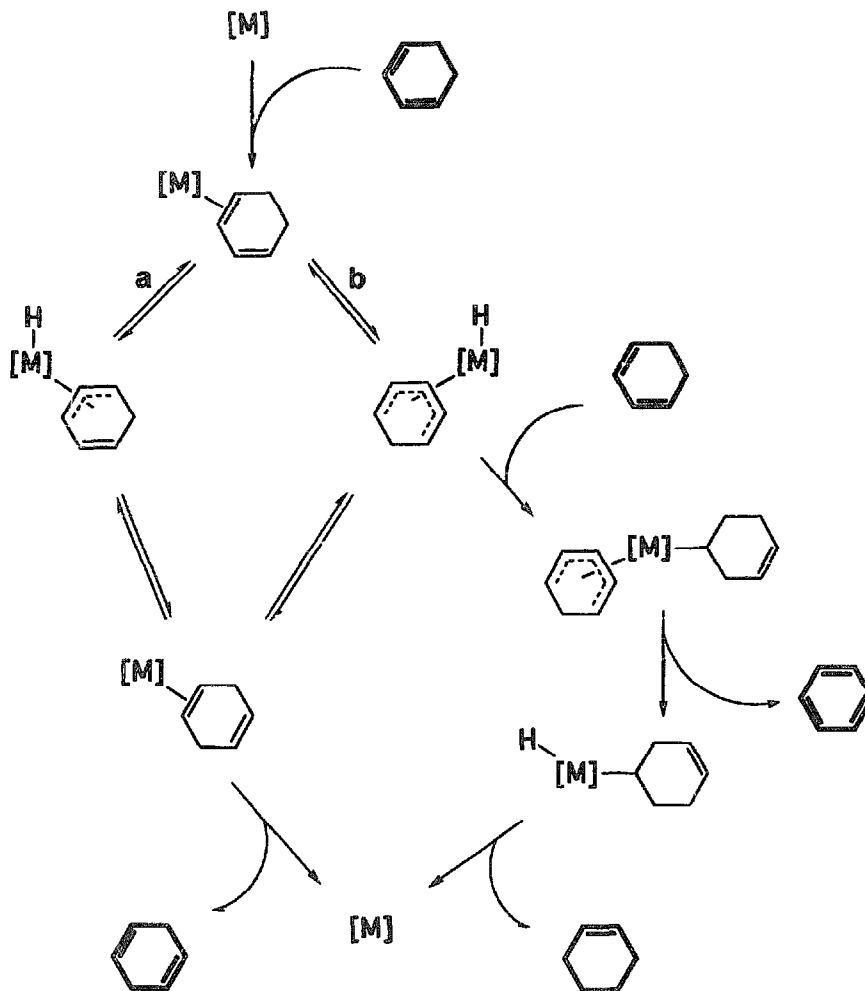
Starting from 1,4- or 1,3-cyclohexadiene both cases give an equilibrium between the 1,3- and 1,4-isomer in the ratio of nearly two to one. However, here the irreversible disproportionation becomes the dominating reaction with increasing

Table 4  
Isomerization of 1,3-cyclohexadiene



Catalyst	T/t	Conversion	Product distribution [%]			
			1,4	A	B	1,3
(cat:sub = 1:50)	°C/h	[%]				
[Cp <sub>2</sub> Ti(Me <sub>3</sub> SiC≡CSiMe <sub>3</sub> )]	25/3	5	3.0	1.0	0.5	95
	60/3	48	22.5	12.5	12.5	52
	60/24	78	11.0	33.5	33.0	22
[Cp <sub>2</sub> Ti(Me <sub>3</sub> SiC≡C <sup>t</sup> Bu)]	60/3	45	25.5	9.5	9.5	55
[Cp <sub>2</sub> Ti(Me <sub>3</sub> SiC≡CPh)]	60/3	98	–	50.5	44.0 <sup>a</sup>	2
[Cp <sub>2</sub> Zr(thf)(Me <sub>3</sub> SiC≡CSiMe <sub>3</sub> )]	60/3	100	–	55.0	44.5	0
[Cp <sub>2</sub> Zr(py)(Me <sub>3</sub> SiC≡CSiMe <sub>3</sub> )]	60/3	100	–	54.0	45.5	0

<sup>a</sup> 2.5% cyclohexane.



Scheme 3. Possible mechanisms for the competing reactions of cyclohexadienes with metallocenes: (a) isomerization, (b) intermolecular hydrogen transfer.

temperature and prolonged reaction time.

The isomerization of the cyclohexadiene (path a) (Scheme 3) or the intermolecular hydrogen transfer, a disproportionation reaction to cyclohexene and benzene (path b), can proceed. The reaction pathway a for cyclic olefins is hindered due to the unfavourable conformation of the  $\eta^3$ -allyl metal hydride intermediate as discussed above.

Therefore, the coordination of two double bonds and hydrogen abstraction yielding an  $\eta^5$ -hexadienyl hydride according to b seems to be preferred for cyclic dienes [13] (a), especially in the case of conjugated systems as 1,3-cyclohexadiene.

In this reaction stage a protonation of the hexadienyl, which leads to the recovering of

cyclohexadiene, as well as a coordination of an additional diene molecule is possible.

The protonation can take place at the central carbon atom (to 1,4-dihydro-benzene) respectively at the end carbons of the  $\eta^5$ -dienyl moiety (to 1,2-dihydro-benzene). The kinetically favoured regioselectivity seems to be at the central carbon atom due to its greater electron density, even though the protonation of an 'end carbon' leads to the thermodynamically more stable product. By this, the ratio of 1,3- to 1,4-cyclohexadiene is sensitive to the specific reaction conditions.

The  $\eta^5$ -hexadienyl hydride intermediate can also coordinate a second diene molecule followed by an intermolecular hydrogen transfer (Scheme 3). As a result cyclohexene and the thermodynamically highly stable benzene are formed.

Surprisingly, contrary to the isomerization of aliphatic olefins the complex  $[\text{Cp}_2\text{Ti}(\text{Me}_3\text{SiC}\equiv\text{CPh})]$  show a deviating behaviour to the other titanocene complexes, since it is more active in transfer hydrogenation, but isomerization products were not detected. The zirconocene complexes are practically inactive in isomerizations of aliphatic olefins as well as of cyclic olefins and the reaction with cyclohexadienes only leads to formation of benzene and cyclohexene. The difference in the activity between titanocene and zirconocene could be explained by the larger atomic radius of Zr which, in contrast to Ti, allows coupling reactions [7,11]. Only for aliphatic olefins is the formation of stable zirconacyclopentene or zirconacyclopentane complexes by coupling reactions of the alkyne ligand and an olefin or of two olefins possible and prevents the isomerization. For cycloolefins a coupling reaction is impossible for both metals but an additional coordination of a second cyclohexadiene and the subsequent intermolecular hydrogen transfer (Scheme 3) can be realized only for Zr.

Additionally, in contrast to isomerizations with titanocene complexes, the zirconocene complexes could not be recovered unchanged from the reaction mixture.

The hydrogen balance found for some reactions and the differences from the expected equimolar benzene–cyclohexene ratio are explained by the formation of a small amount of dihydrogen during the reaction (not detected) in particular for zirconium catalysts or the hydrogenation of cyclohexadiene to cyclohexane (see Table 3 and Table 4 for  $[\text{Cp}_2\text{Ti}(\text{Me}_3\text{SiC}\equiv\text{CPh})]$ ) giving less cyclohexene than benzene.

In conclusion, titanocene alkyne complexes are effective catalysts for the isomerization of olefins in a short period without any byproducts. The simple method of generating the free metallocene unit under mild conditions makes the  $\text{Cp}_2\text{M}$  species accessible for synthetic use.

Further investigations are directed at extending this metallocene-mediated isomerization to functionalized olefins, which possibly are of interest in industrial application. Additionally it should be

proved whether cyclohexadienes in cooperation with metallocenes can act as hydrogen donors and thus these systems are utilizable in hydrogenations of other substrates under mild conditions.

### 3. Experimental

All operations were carried out in an inert atmosphere (argon) with standard Schlenk techniques. Olefins were treated with sodium tetraethylaluminate, distilled, and stored under argon. The following spectrometers were used: NMR, Bruker ARX 300, IR, Nicolet Magna 500 (Nujol mulls using KBr plates), GC, Hewlett Packard 5890 with FID detector.

#### 3.1. Isomerization reaction

A typical reaction was performed as follows. A Schlenk tube (50 ml) was charged with the alkyne complex ( $\sim 0.2$  mmol) and a corresponding amount of the olefin (cat:sub = 1:50) under argon. The mixture was stirred at the temperature given in Tables 1–4. The reaction was terminated by cooling the mixture down to  $-78^\circ\text{C}$ , and volatile products were evaporated in vacuo. The distillate was identified (NMR) and quantitatively determined by gas chromatography. The crystalline residue was characterized by IR spectroscopy. Product distribution and yields are presented in Tables 1–4.

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