Metathesis of Renewable Polyene Feedstocks - Indirect Evidences of the Formation of Catalytically Active Ruthenium Allylidene Species

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Abstract

Cross-metathesis (CM) of conjugated polyenes, such as 1,6-diphenyl-1,3,5-hexatriene (**1**) and α-eleostearic acid methyl ester (**2**) with several olefins, including 1-hexene, dimethyl maleate and *cis*-stilbene as model compounds has been carried out using (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)-dichloro(*o*-isopropoxyphenylmethylene)ruthenium (Hoveyda-Grubbs 2nd generation, **HG2**) catalyst. The feasibility of these reactions is demonstrated by the observed high conversions and reasonable yields. Thus, regardless of the relatively low electron density, =CH–CH= conjugated units of molecules, including compound **2** as a sustainable, non-foodstuff source, can be utilized as building blocks for the synthesis of various value-added chemicals via olefin metathesis. DFT-studies and the product spectrum of the self-metathesis of 1,6-diphenyl-1,3,5-hexatriene suggest that a Ru η^1-allylidene complex is the active species in the reaction.
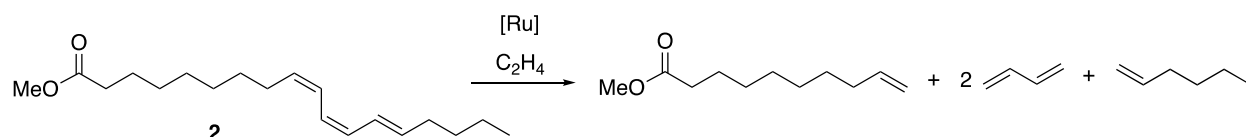
1. Introduction

Biological materials containing conjugated bonds, such as conjugated polyunsaturated fatty acids, terpenes and chromophores, are abundant in nature.[1] Polyenes are highly unsaturated conjugated compounds with characteristic color and antioxidant properties.[2] They have a wide range of applications, including molecular wires in nano-devices and "light harvesting materials" in photosynthesis.[3] These chemicals are often underutilized as renewable feedstock because of their special conjugated electron systems. This is especially true for their use in metathesis reactions, as the available catalyst systems have not been optimized yet to conjugated compounds. Olefin metathesis is fundamentally one of the most versatile synthetic methodologies in homogeneous catalysis and it has initiated new industrial avenues leading to innovative materials, petrochemicals and pharmaceuticals since its invention about half a century ago.[4] In the last twenty years many chemical technologies have been developed on the basis of olefin metathesis, which also became dominant in several sustainable and green chemical processes.[5] The application of olefin metathesis in the field of green chemistry, especially in the utilization of renewable feedstocks, is emerging.[6]

Even though many transition metals were found to catalyse metathesis reactions, the most widely used and investigated systems still employ Ti, W, Mo and Ru. The latter has the highest reactivity with olefinic bonds, while remaining tolerant towards moisture, oxygen and several functional groups. To date, Ru appears to be the most frequently selected transition metal for metathesis reactions.[7]

The synthesis of polyenes was carried out mainly by the Wittig reaction in the past.[8] The longest polyene synthetized so far contains eighty carbon atoms and twenty-seven conjugated double bonds.[9] However, research on polyenes and π-conjugated oligomers has dramatically expanded by the development of transition metal catalysed cross-coupling reactions and analytical techniques, allowing the well-designed synthesis of linear, conjugated molecular rods with accurate characterisation.[10] An emerging alternative way for the synthesis of polyenes is the

metathesis of conjugated olefins.[11]

However, not only the fabrication of conjugated systems but also their breakdown into valuable building blocks via olefin metathesis can be substantial. For example, α-eleostearic acid as a carbon-dioxide neutral renewable material, containing three conjugated double bonds (at carbons 9-*cis*, 11-*trans* and 13-*trans*), can be the green alternative for the replacement of important petro-based chemicals such as nylon monomers.[12] One source of such a conjugated compound is tung oil, which is non-edible and can be produced from the seeds of tung plants grown on waste or marginal lands.[13] Unlike other vegetable oils, such as soybean or sunflower oils (containing mainly oleic acid), tung oil consists of the desired α-eleostearic acid in up to 80 % concentration, that makes this bio-based raw material suitable for the synthesis of a wide range of chemicals via olefin metathesis. For example, the simple ethenolysis of α-eleostearic acid can provide methyl dec-9-enoate and C4–C10 hydrocarbons including butadiene and 1-hexene (Scheme 1). These chemicals are widely used as additives in cosmetics and in the production of synthetic rubber or high- and low density polyethylene (HDPE/LDPE).[14] The cross metathesis of conjugated polyenes is an alternative way for the utilization of =CH–CH= building blocks for the synthesis of many other value added chemicals.
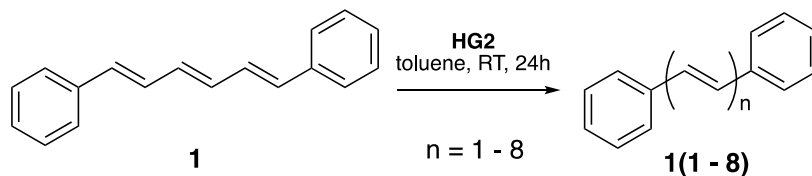

Scheme 1. Tentative scheme of ethenolysis of α-eleostearic acid methyl ester (**2**)

In this short communication, we are reporting our preliminary results on the synthetic and mechanistic investigation of the ruthenium catalysed metathesis reactions of polyenes using 1,6-diphenyl-1,3,5-hexatriene (**1**) and α-eleostearic acid methyl ester (**2**) as model compounds.

2. Synthesis of polyene homologs

The self-metathesis of 1,6-diphenyl-1,3,5-hexatriene (**1**) has been investigated in toluene solution using Hoveyda-Grubbs 2nd (**HG2**) generation catalyst at room temperature. During the reaction, the colour of the mixture changed gradually from green to orange, meanwhile the formation of a precipitate was observed. The precipitation may occur due to the formation of $n > 3$ homologs, which are expected to have lower solubility than the $n \leq 3$ species. It is well-known that the solubility of polyacetylene decreases steadily with the chain growth of the oligomer.[15] As the reaction mixtures could not be investigated in one pot because of the precipitation, the components were hydrogenated off to obtain fully soluble, saturated α,ω-phenyl substituted hydrocarbon chains. Then, assuming that the components of the reaction mixture retain comparative response factors, GC-MS analyses were carried out and the approximate values of the conversion and yields were estimated from the peak areas of the total ion current (TIC) chromatograms. These indicated a relatively high conversion of the starting material **1** (92%) and the formation of **1(1-6)** compounds in reasonable yields of (**1(1)**: 20%; **1(2)**: 21%; **1(5)**: 25%; **1(6)**: 15%). Homologs **1(4)**, **1(7)** and **1(8)** were also detected in traces. (Scheme 2, Figure 1)

Scheme 2. Self metathesis of **1**, synthesis of polyene homologs via olefin metathesis.
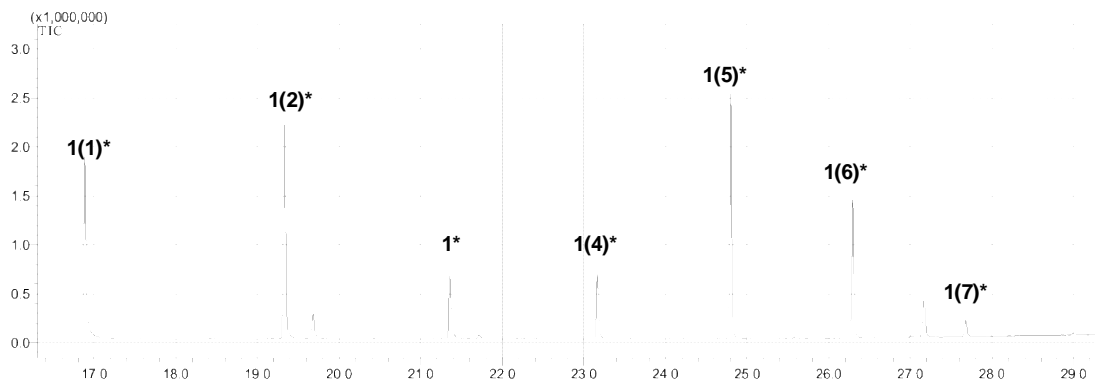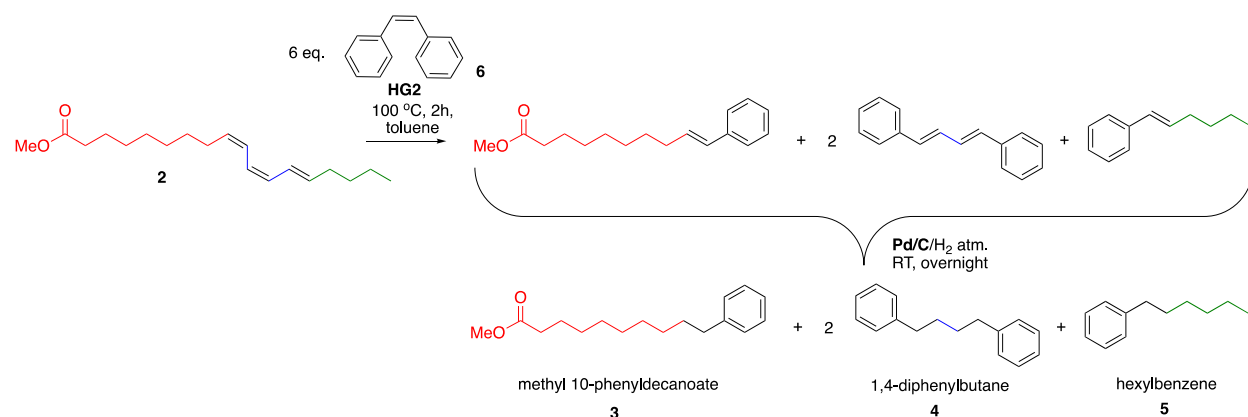
Figure 1. Total ion current (TIC) chromatogram plot of the hydrogenated self-metathesis reaction mixture of **1** using **HG2** catalyst. (*hydrogenated derivatives)

3. Cross-Metathesis (CM) of conjugated feedstocks

The cross-metathesis (CM) of **1** with 1-hexene and dimethyl maleate using **HG2** has also been investigated. In the case of 1-hexene, a high (more than 90%) conversion of **1** was estimated as judged by the TIC chromatogram (Figure S9). The reaction mixture contained a wide range of hydrocarbons, including the expected alkylated benzenes (see supplementary material) as major products. However, the reaction of **1** with dimethyl maleate under the same condition revealed a rather low conversion with only the formation of the self-metathesis products of **1** (Figure S7).

Following the preliminary studies described above, the metathesis of α-eleostearic acid methyl ester (**2**) as a potential renewable material was investigated. The self-metathesis of **2** followed by one-pot hydrogenation has revealed the formation of the expected reaction products including hydrocarbon and methyl ester homologs with reasonable yields (Figure S10). The feasibility of the CM of **2** has been investigated with *cis*-stilbene (**6**) as a model compound. Compound **6** is an ideal choice for a cross-coupling agent, as new side products are not provided in the self-metathesis and the core structure of the active species is not affected in a reaction with the catalyst. Thus, the rate and conversion of the CM reaction between **2** and **6** is supposedly determined solely by **2**.

The reaction mixtures were hydrogenated off on Pd/C in all cases to improve the solubility of the components by saturation. Furthermore, by the elimination of the presence of Z and E isomers of the reaction products, the chromatograms could be simplified. The CM reaction of **2** with **6** followed by hydrogenation led to the formation of methyl 10-phenyldecanoate (**3,** 95%), 1,4-diphenylbutane (**4**, 35%) and hexylbenzene (**5**, 95%) as major products (Scheme 3, Figure 2). The yield was determined by quantitative ^{13}C NMR.[16]

Scheme 3. Cross-metathesis (CM) of α-eleostearic acid methyl ester (**2**) with *cis*-stilbene (**6**).
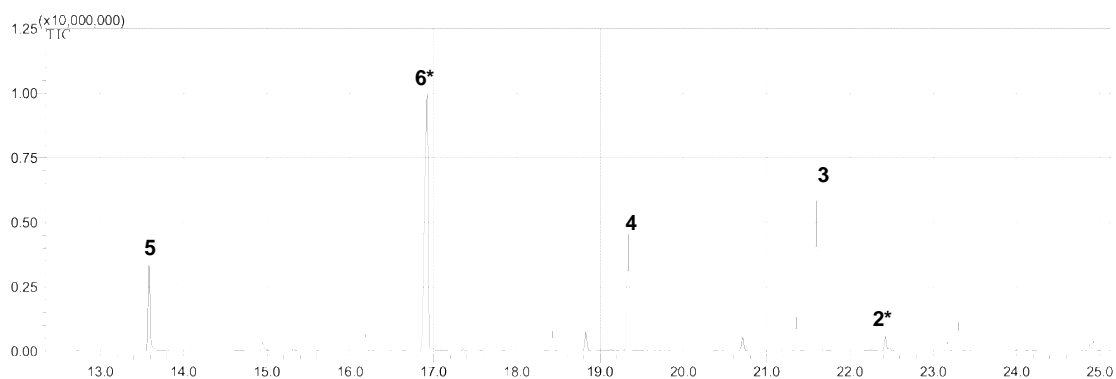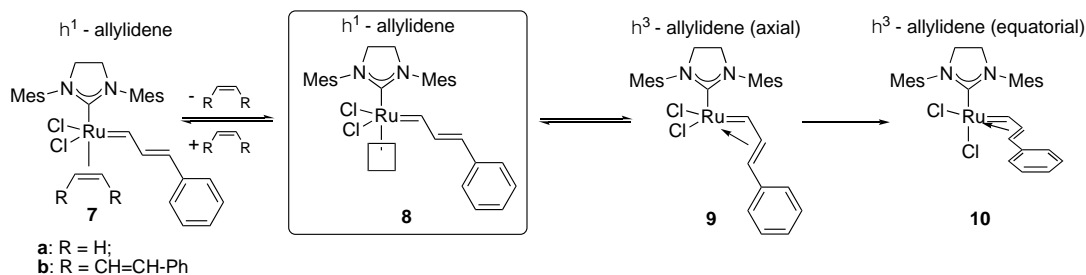

Figure 2. TIC chromatogram of the CM reaction mixture of **2** and **6**. (*hydrogenated derivatives)
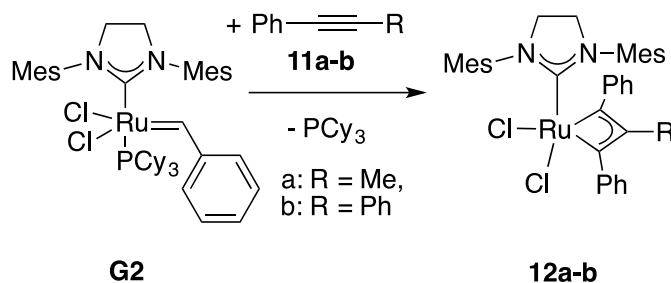
4. Mechanistic Considerations

The product spectrum of the self-metathesis of **1** suggests that a Ru η^1-allylidene complex (**8**) is the active species in the reaction (Scheme 4). However, there is some concern about the possible deactivation of the η^1 species by transformation into inactive η^3 structures **9** and/or **10,** based on earlier studies. In these complexes the π-bond of the allyl moiety also coordinates to the Ru atom, occupying an equatorial and an axial (**9**) or two equatorial (**10**) coordination sites (Scheme 4). Specifically, a stable and catalytically inactive analogue of **10** has been reported by Grubbs and co-workers.[17]
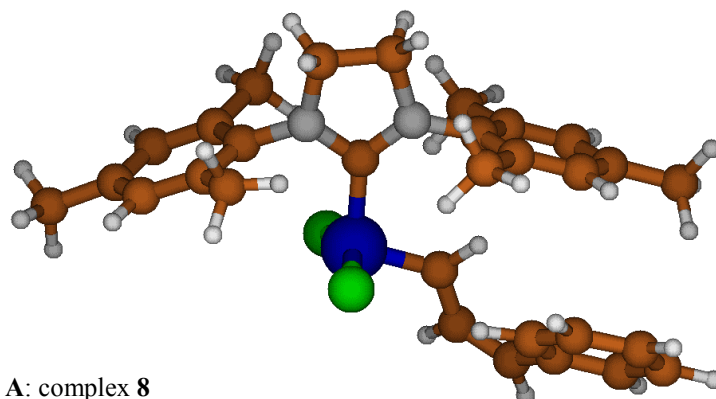
-6-

Scheme 4. Hypothetic competition between **7** and/or **9** and/or **10**

They have synthetized complex **10** by the reaction of Grubbs 2nd generation (**G2**) catalyst with phenyl acetylenes (Scheme 5), and found an unusual chlorine arrangement around the Ru atom. The η^1 - η^3-allylidene conversion was investigated and the η^1-allylidene species formation was not observed even at 130 $^{\circ}$C. One of the chlorine atom is almost perpendicular to the Cl–Ru=CR'R" plane in the suggested structures. However, according to recent X-Ray studies, the highly active (i.e. $Cl_2Ru=CHPh$ or $Cl_2Ru=CH_2$) catalyst species contains both the chlorines in equatorial positions close to planar with the carbene (=CHP or $=CH_2$) ligands.[18] The shift of one of the Cl atoms to axial position may explain the catalytic inactivity of the stable allyl η^3-triphenyl-allylidene structure.
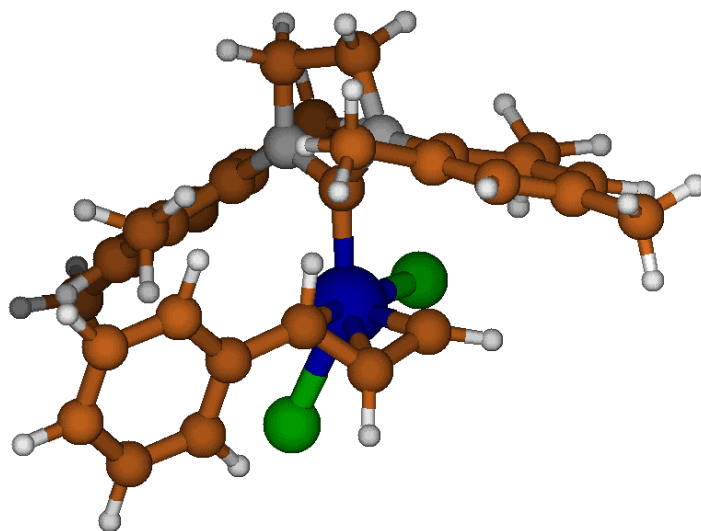

Scheme 5. Formation of η^3-allylidene Ru NHC complex based on the study by Trnka and Grubbs[17]
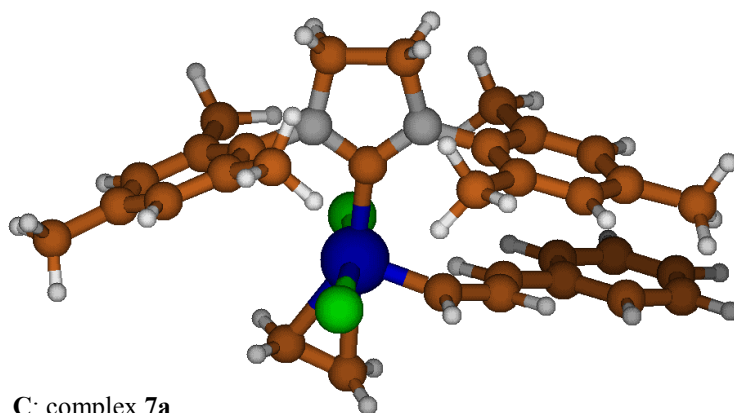
In order to understand the possibility of inhibition by conversion of the active η^1 species (**8**) to η^3-allylidene structures (**9**) and/or **10**, we used methods of electronic structure theory, and calculated the molecular geometries and relative energies of the candidate species.[19] Density functional theory was used in the calculations at the M06/LANL2DZ level proposed by Zhao and Truhlar[20] as appropriate to describe Grubbs catalysts, and with the CAM-B3LYP functional combination using the basis sets SDD (for Ru, including also the pseudopotential describing the core electrons) and 6-31G (d,p) (for C, N, H). Both functionals handle the dispersion effects properly that are essential in the formation and energetics of various isomers and conformers of the catalyst. As a test, we calculated the geometry of the triphenyl analog of **10** reported by Grubbs and co-workers, and found that both methods provide very good agreement with the X-ray structure. With the validated methods, we searched for the candidate structures, and identified several conformers of the η^1 species, differing only in the orientation of the allyl moiety and of the phenyl substituent. The most stable conformer of complex **8** is structure **A** shown in Figure 3. In addition to this, a η^3 species **10** with an equatorial and an almost axial Cl atom (**B** in Figure 3) has also been found at a realistic relative energy level (Figure 4). None of our efforts led to success in finding structure **9** with π coordination at the axial position of Ru. The structures and binding energies of the adduct **7** of **8** with olefins, C_2H_4 or **1** have also been determined, (**C** in Figure 3).

A: complex **8**

B: complex **10**

C: complex **7a**

Figure 3. Calculated DFT structures for complexes **7a**, **8** and **10**.

The relative energies of the complexes are shown in Figure 4 (the relative free energies at 300 K are essentially the same). The energy of **10** is referenced to that of **8**, while the energy of adduct **7** is measured from the sum of those of complex **8** and the olefin. One can see that the olefin coordination is highly exothermic, while formation of the η^3 structure is endothermic by more than 40 kJ/mol. It is remarkable that the binding energy of the complex of **8** and **1** is significantly larger than that of **8** and ethylene. It can be concluded from the energetics that catalysts deactivation by the formation of a η^3 species should not be significant when a 3-phenylallylidene group is present (Figure 4). This is in good agreement with the observation mentioned earlier, namely, that the self-metathesis of **1** proved to be facile.
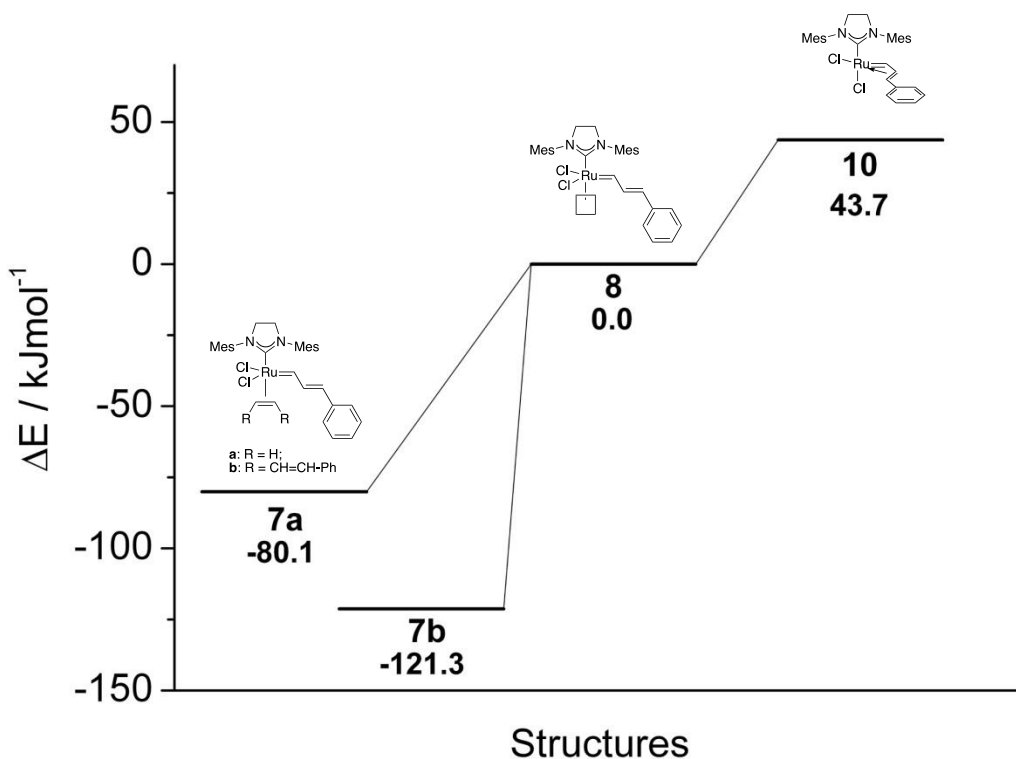

Figure 4. The relative energies of complexes **7a**, **7b, 8** and **10**.

5. Summary

In summary, this paper covers the results of an exploratory study on the metathesis of polyenes including a renewable material. It can be concluded that the polyenes containing three olefinic bonds undergo metathesis reaction despite the relatively low electron density on the conjugated double bonds. Thus, a sustainable, non-foodstuff material such as α-eleostearic acid can be converted into valuable chemicals. The electronic structure theory calculations showed that catalyst deactivation is negligible for the ruthenium 3-phenyl-allylidene system, because the formation of the possible inactive η^3 species (**10**) is endothermic, while the addition of the next olefin to the Ru (**7a** and **7b**) is highly exothermic. The equilibrium is essentially shifted towards the ruthenium η^1- allylidene-olefin complexes (**7a** and **7b**).

Acknowledgement

Associated Content

Supporting Information. Experimental procedures and characterization data. This material is available free of charge via the Internet at http://www.sciencedirect.com

References

[1]   (a) N. Fontan, M. Dominguez, R. Alvarez, A.R. de Lera, Eur. J. Org. Chem. 2011 (2011) 6704; (b) J. Wu, T. Zhang, G. Ma, P. Li, L. Ling, B. Wang, J. Appl. Polym. Sci. 130 (2013) 4201; (c) N. Shinohara, T. Tsuduki, J. Ito, T. Honma, R. Kijima, S. Sugawara, T. Arai, M. Yamasaki, A. Ikezaki, M. Yokoyama, K. Nishiyama, K. Nakagawa, T. Myazawa, I. Ikeda, Biochim. Biophys. Acta. 1821 (2012) 980; (d) D.J. Crumb, D.A. Vattem, Int. J. Appl. Res. Nat. Prod. 4 (2011) 12; (e) A. Behr, H. Witte, Z. Bayrak, Eur. J. Lipid Sci. Technol., 115 (2013) 721; (f) S. Zhu, Y. Wu, Synlett 25 (2014) 26; (g) Y. Kobayashi, S. Yoshida, Y. Nakayama, Y. Eur. J. Org. Chem. 2001 (2001) 1873.

[2]   (a) S.R. Marder, W.E. Torruellas, M. Blanchard-Desce, V. Ricci, G.I. Stegeman, S. Gilmour, J.-L. Brédas, J. Li, G.U. Bublitz, S.G. Boxer, Science 276 (1997), 1233; (b) R.F. Service, Science 276 (1997) 1195.

[3]   T. Ritz, A. Damjanovic, K. Schulten, J.-P. Zhang, Y. Koyama, Photosynth. Res. 66 (2000) 125.

[4]   A.H. Hoveyda, A.R. Zhugralin, Nature 450 (2007) 243.

[5]   A.M. Rouhi, C&EN 80 (2002) 29.

[6]   J.C. Mol, Green Chem. 4 (2002) 5.

[7]   R.H. Grubbs, Ed.; *Handbook of Metathesis*, Wiley/VCH, Weinheim, 2003.

[8]   H. Ernst, Pure Appl. Chem. 74 (2002) 1369.

[9]   M. Zeeshan, H.-R. Sliwka, V. Partali, A. Martínez, Organic Lett. 14 (2012) 5496.

[10]   R.E. Martin, F. Diederich, Angew. Chem. Int. Ed. 38 (1999) 1350.

[11]   D. Tao, K.B. Wagener, Macromolecules 27 (1994) 1281.

[12]   Noordover, B.A.J. "Polyesters, polycarbonates and polyamides based on renewable

resources" V. Mittal (Ed.), Renewable Polymers: Synthesis, Processing, and Technology, Jonh Wiley & Sons, Inc., Hoboken, NJ, USA (2011).

[13] Q. Shang, W. Jiang, H. Lu, B. Liang, Bioresour. Technol. 101 (2010) 826.

[14] J.C. Mol, Topics in Catal. 27 (2004) 97.

[15] C.B. Gorman, E.J. Ginsburg, R.H. Grubbs, J. Am. Chem. Soc. 115 (1993) 1397.

[16] Quantitative NMR specification and synthetic procedure is described in the supplementary material.

[17] T.M. Trnka, M.W. Day, R.H. Grubbs, Organometallics 20 (2001) 3845.

[18] (a) R. Tuba, E.N. Brothers, J.H. Reibenspies, H.S. Bazzi, J.A. Gladysz, Inorg. Chem. 51 (2012) 9943; (b) T.E. Schmid, X. Bantreil, C.A. Citadelle, A.M.Z. Slawin, C.S.J. Cazin, Chem. Commun. 47 (2011) 7060; (c) M.L. Macnaughtan, M.J.A. Johnson, J.W. Kampf, Organometallics 26 (2007) 780; (d) S.Y. Yun, M. Kim, D. Lee, D.J. Wink, J. Am. Chem. Soc. 131 (2009) 24.

[19] Electronic structure calculations were performed with Gaussian 09. The nature of the optimized minima was checked by calculating the eigenvalues of the Hessian matrix. The reported structures are characterized by purely positive eigenvalues.
M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R.

Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, and D.J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.

[20]   Y. Zhao, D.G. Truhlar, J. Chem. Theory Comput. 5 (2009) 324.