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CATALYTIC TRANSFORMATION OF SEED OIL DERIVATIVES *VIA* OLEFIN METATHESIS

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SUMMARY

Unsaturated fatty acid esters derived from seed oils undergo metathesis at the C=C bond to give new internal and terminal olefins of interest in chemical manufacturing. The key to realizing this industrial opportunity is the ability to deploy catalysts that tolerate functional groups and remain reactive towards internal olefins even at high conversions. Recent developments in catalyst and reactor design are bringing these targets closer to commercial reality.

Key words: unsaturated fatty acid esters, renewable feedstocks, seed oils

INTRODUCTION

Recent dramatic increases in the price of crude oil have presented the world's chemical industry with an opportunity and an obligation to investigate the use of renewable rather than fossil-based feedstocks for the manufacture of chemical intermediates and materials. Fatty acid esters derived from seed oils are an appealing alternative source of chemicals, since their chemical structures are closely related to those of the hydrocarbons in crude oil. The use of seed oil-based feedstocks in environmentally benign and sustainable chemical manufacturing has the potential to reduce net CO_2 emissions and produce non-toxic materials that are also biodegradable. Single component or high purity feedstocks are preferred, because chemical separations are generally energy- and capital-intensive. Thus high oleic sunflower oil, with an oleate content after transesterification approaching 90%, is particularly well-suited as a renewable chemical feedstock.

Traditionally, almost all reactions of seed oils were conducted at the ester functionality, with the exception of hydrogenation which eliminates the C=C double bond (Baumann *et al.*, 1988). In recent years, many other reactions at this site have been explored (Biermann *et al.*, 2000). Olefin metathesis, in which substituents of the double bond are exchanged, is considered a desirable technology because it is

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highly atom-efficient. The reaction leads to the formation of new olefinic compositions (Figure 1).

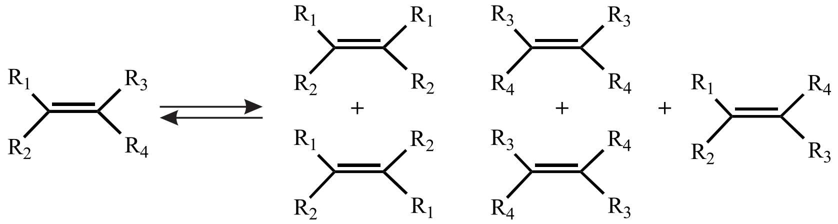


Figure 1: Redistribution of olefinic substituents via the metathesis reaction

The nature of the products obtained depends on the type of olefinic substrate: acyclic monounsaturated substrates give acyclic olefins (simple metathesis), α,ω-unsaturated dienes and strained cyclic olefins give polymers (acyclic diene metathesis polymerization, ADMET, and ring-opening metathesis polymerization, ROMP), some dienes give unstrained rings by extrusion of ethylene (ring-closing metathesis, RCM) and cycloolefins may give larger cycloolefins (ring-expanding metathesis). For all these reactions, the universal Chauvin mechanism involves [2+2] cycloaddition of the olefin substrate to a metal carbene catalyst, followed by cycloreversion of the metallacyclobutene intermediate (Figure 2).

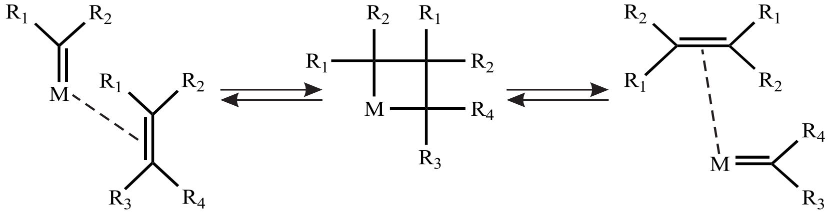


Figure 2: Mechanism of catalytic olefin metathesis via alternation of the metal carbene and metallacyclobutane propagating intermediates

In principle, olefin metathesis is highly selective. However, side-reactions such as olefin isomerization are common, and deactivation has been a major problem with existing catalyst technology.

Self-metathesis of fatty acid methyl esters (FAMEs)

Self-metathesis, or homometathesis, requires no reagent other than the olefin itself. Thus homometathesis of the FAME methyl oleate yields an unsaturated diester, dimethyl-9-octadecene-1,18-dioate, and an internal olefin, 9-octadecene (Figure 3).

One potential application for homometathesis is the reformulation of biodiesel, in order to enhance its viscosity and lubricity without compromising stability or biodegradability (Holser *et al.*, 2006). A second application is the production of polymers. Long chain dicarboxylic acid esters were shown to undergo condensation polymerization at 150-200°C with diols such as ethylene glycol, 1,4-butanediol and 1,4-bis(hydroxymethyl)cyclohexane, in the presence of a Lewis acid catalyst, $Ti(O^{t}Bu)_4$ (Warwel *et al.*, 2001). Unlike their petroleum-based aromatic analogues, the resulting aliphatic polyesters are biodegradable. Finally, olefin metathesis is a key reaction in the catalytic formation of macrocycles. Homometathesis of ethyl oleate to give diethyl-9-octadecene-1,18-dioate was followed by cyclization *via* the Dieckmann condensation, ester hydrolysis and decarboxylation to 9-cycloheptadecen-1-one (Tsjui and Hashiguchi, 1981). By an alternate route, cyclization by RCM of oleon (pentatriaconta-9,26-dien-18-one), the product of Claisen condensation of methyl oleate, gives the same macrocycle (Plugge and Mol, 1991). Although neither synthetic route is stereoselective, the *cis*-isomer of the macrocyclic ketone is the valuable musk ingredient civetone.

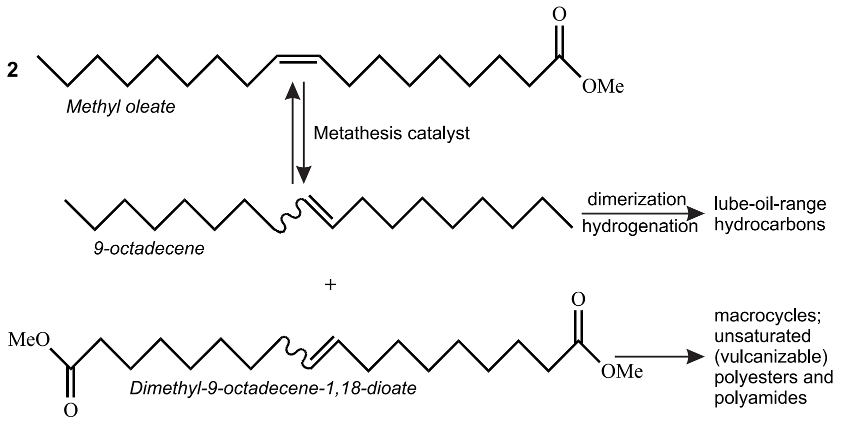


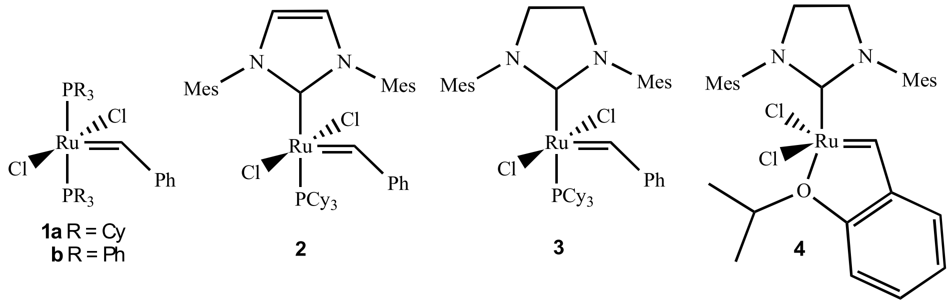
Figure 3: Homometathesis of methyl oleate

Metathesis catalysts for FAMEs

The presence of an ester group in the olefinic substrate makes it essential to use a catalyst that tolerates functional groups and is active at moderate reaction temperatures in the liquid phase. The former requirement rules out high-valent, single-component homogeneous catalysts based on Mo and W, while the latter rules out unpromoted heterogeneous catalysts based on supported metal oxides of these metals. The first report of methyl oleate self-metathesis involved a two-component homogeneous catalyst, $WCl_6/SnMe_4$ (Van Dam *et al.*, 1972), in which the active metal (W) was likely reduced from its maximum oxidation state by the alkyltin promoter. The same catalyst system was also reported to catalyze the homometathesis of glyceryl trioleate, yielding octadec-9-ene and dicarboxylic acid glyceryl esters. Subsequently, the diene methyl linolate and the triene methyl linolenate were shown to react over the same homogeneous catalyst to give cyclohexa-1,4-diene by RCM, as well as acyclic alkenes and unsaturated mono- and dicarboxylic esters

(Verkuijlen and Boelhouwer, 1974). A heterogeneous catalyst for these reactions, $SnMe_4$-promoted Re_2O_7/Al_2O_3, was discovered shortly afterwards (Verkuijlen *et al.*, 1977). It was proposed that the role of the alkyltin promoter is reduction of high-valent Re(VII) (Xiaoding *et al.*, 1985).

Catalysts based on late transition metals (Groups 8-10 in the Periodic Table) are more stable in low and intermediate oxidation states, and they tend to be more tolerant of substrate functionality. In one of the earliest reports, a 4:1 mixture of AgO_2CCF_3 and $[Ir(coe)Cl]_2$ (coe is cyclooctene) catalyzed the selective homometathesis of 10 equiv. methyl oleate to octadec-9-ene and the unsaturated diester, accompanied by small amounts of products derived from isomerization (France *et al.*, 1994). The AgO_2CCF_3 was suggested to abstract chloride and oxidize Ir(I) to Ir(III). More recent studies of homogeneous FAME metathesis reactions have focused on single-component, isolable Ru-based catalysts, known as Grubbs' catalysts (Figure 4). The first generation of these catalysts, which bear two bulky trialkylphosphine ligands (**1**), have low thermal stability at 50°C and low reactivity towards internal olefins. Catalyst stability is also generally poor at low loadings, limiting opportunities for commercial applications in which high turnovers are required. Thermal stability is much improved in the second-generation catalysts **2** and **3**, in which one phosphine ligand is replaced by an N-heterocyclic carbene ligand such as 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes). The second generation catalysts also show higher activity, especially for functionalized and internal olefins (Weskamp *et al.*, 1998), although often at the expense of selectivity. Thus catalyst **3** showed a productive turnover number for methyl oleate homometathesis of 440,000 at 55°C, compared to 2,500 for catalyst **1a** (Dinger and Mol, 2002). New first-generation Grubbs' catalyst with phosphanabicyclononane (Phoban) ligands show improved thermal stability while retaining very high selectivity for the self-metathesis of methyl oleate (Forman *et al.*, 2004).



1a R = Cy
b R = Ph

2

3

4

*Figure 4: Typical Grubbs' first generation (**1a,b**) and second generation (**2-4**) catalysts.*

A major drawback in the use of homogeneous metathesis catalysts for large-scale processes is the high cost of catalyst separation and recovery. Incomplete catalyst removal leads to undesirable product isomerization during product purification; furthermore, the ability to use low conversion with recycle to surpass equilibrium-limitations to conversion is difficult with a homogeneous catalyst. Catalyst decomposition products lead to loss of selectivity due to side-reactions at high turnovers, particularly during recycle (Dinger and Mol, 2002). Immobilizing homogeneous ruthenium catalysts onto a solid support, such as functionalized polystyrene-divinylbenzene, can extend their lifetimes but is accompanied by considerable loss of activity (Nguyen and Grubbs, 1995) and/or pronounced leaching (Nieczypor *et al.*, 2001). A supported organometallic catalyst obtained by grafting $Re(\equiv C^tBu)(=CH^tBu)(CH_2{}^tBu)_2$ onto silica gave 900 turnovers in the homometathesis of methyl oleate (Chabanas *et al.*, 2003), however, like the homogeneous catalysts, it is intrinsically non-regenerable and therefore far below the threshold for commercial viability. Since the products of seed oil homometathesis are not volatile enough to be removed by vaporization, one possible solution to the separation problem is the use of size-selective membranes. A reactor equipped with a polyimide nanofiltration membrane to reject the homogeneous catalyst and its decomposition products has been proposed for continuous recycle operation (Burdett *et al.*, 2006).

Although preferred for large-scale industrial processes, heterogeneous metathesis catalysts show much lower effective turnover numbers for FAMEs than most homogeneous catalysts, and particularly in comparison to the newest Grubbs' catalysts. For example, one of the best heterogeneous formulations is Re_2O_7 supported on borated silica-alumina. The addition of a promoter, typically an organotin compound such as $SnBu_4$, is required in order to prevent catalyst deactivation by polar functional groups. The promoted catalyst gave 198 turnovers in methyl oleate self-metathesis (Buffon *et al.*, 2002). While heterogeneous metathesis catalysts have the advantage of being readily reactivated by calcination when the promoter is absent, the buildup of SnO_2 after repeated additions of SnR_4 interferes with active site regeneration (Spronk and Mol, 1991). The search for a tin-free catalyst is also driven by the toxicity of organotin promoters. A hypothesis that alkyltin compounds cause *in situ* generation of organorhenium(VII) trioxides was supported by the finding that a tin-free catalyst active in methyl oleate self-metathesis can be prepared by deposition of $MeReO_3$ onto silica-alumina (Herrmann *et al.*, 1991). Recently, $MeReO_3$ formation was predicted computationally and observed spectroscopically in a $SnMe_4$-promoted perrhenate catalyst (Moses *et al.*, 2006). The mechanism of activation of $MeReO_3$ by the support involves Lewis acid-base interactions between the oxo ligands and distorted four-coordinate aluminum sites, as well as between Re(VII) and support oxygen atoms (Moses *et al.*, 2006). These interactions may reduce the barrier for tautomerization of the methyl ligand to a carbene capable of initiating olefin metathesis, although reduction of Re(VII) has not been excluded.

FAME cross-metathesis

Cross-metathesis is performed in the presence of a second olefin, typically an acyclic olefin with symmetrical double-bond substituents. It can result in chain lengthening or chain shortening, depending on the choice of olefin. Cross-metathesis of methyl oleate with a light olefin leads to the more valuable detergent-range FAMEs. The ideal cross-metathesis reaction from an economic standpoint is ethenolysis, leading to 1-decene and methyl-9-decenoate. In principle, this reaction is not equilibrium-limited: it can be driven to completion simply by the use of a high pressure of ethylene (Figure 5). Terminally-unsaturated methyl esters are precursors for polymers including polyesters, polyethers and polyamides, and they can be copolymerized with α-olefins to yield functionalized polyolefins. The α-olefins can be used as detergent precursors and as comonomers for polyolefins. Cross-metathesis with a cyclic olefin C_nH_{2n} is also possible, and can be used to extend the carbon chain by *n* units. For example, the reaction of methyl oleate with cyclododecene gave the unsaturated ester $CH_3(CH_2)_7CH{=}CH(CH_2)_{10}CH{=}CH(CH_2)_7CO_2CH_3$ which, after catalytic reduction, yielded the plant growth hormone triacontanol $CH_3(CH_2)_{28}CH_2OH$ (Villemin, 1983).

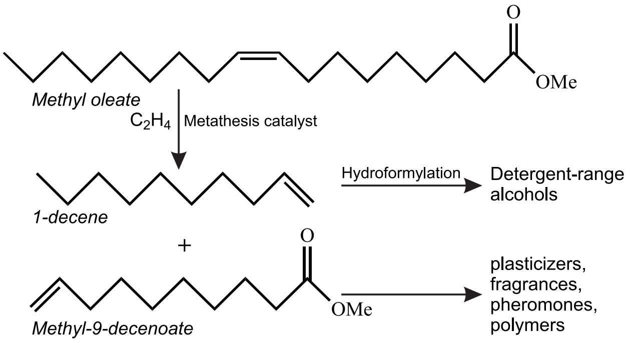


Figure 5: Ethenolysis of methyl oleate

One problem limiting selectivity in metathesis is competing olefin isomerization (migration of the C=C bond), particularly at high turnovers and with the second-generation Grubbs' catalysts (Janse van Rensburg *et al.*, 2004). Isomerization is catalyzed by the metathesis catalyst or one of its decomposition products. In the case of the Grubbs' catalysts, the culprit was shown to be a ruthenium hydride (Hong *et al.*, 2004). Isomerization was suppressed by the addition of 1,4-benzoquinone, which was reduced to hydroquinone by the metal hydride (Hong *et al.*, 2005). Addition of a phenol (500 equiv. per Ru) enhanced catalyst lifetime ten-fold in a first-generation Grubbs' catalyst, and increased selectivity in a second-generation Grubbs' catalyst, allowing higher substrate/catalyst ratios in cross-metathesis and conferring resistance to degradation by feedstock impurities such as ketones, alcohols, aldehydes, alkynes, dienes and peroxides (Forman *et al.*, 2005).

Heterogeneous metathesis catalysts tend to be highly selective in FAME cross-metathesis. Warwel *et al.* (2001), converted 600 equiv. FAMEs from high oleic sunflower oil to 1-decene and methyl-9-decenoate (>80% recovered yield) by reaction with 50 bar ethylene at 20°C for 2 h using the heterogeneous catalyst $SnBu_4$-promoted Re_2O_7 supported on borated silica-alumina (Warwel *et al.*, 2001). Copolymerization of the resulting terminally-unsaturated methyl ester with 2.5 bar ethylene at 25°C using a Pd diimine catalyst gave highly branched, functionalized polyethylene with potential application as a compatibilizer for polyolefins and polar polymers (Warwel *et al.*, 2001). Transesterification of the unsaturated methyl ester with a diol gives an α,ω-alkylene dialkenoate, which undergoes ADMET polymerization over $SnBu_4$-promoted Re_2O_7/borated silica-alumina. Reaction of methyl oleate with excess 1-hexene suppresses undesired homometathesis to give, selectively, 3-dodecene and methyl-9-dodecenoate (Mol, 2002). Cis-trans isomerization of methyl oleate was not a problem in batch reactor tests. However, buildup of the trans isomer, which undergoes metathesis more slowly, could become an issue in a continuous reactor with catalyst recycle (Burdett *et al.*, 2004).

Commercial viability for methyl oleate cross-metathesis is predicated on obtaining a minimum of 50,000 turnovers (Burdett *et al.*, 2004). The limited number of turnovers reported in many catalyst systems for ethenolysis of methyl oleate (Warwel *et al.*, 2001; Dinger and Mol, 2002) has been attributed to the production of terminal olefins, which engage in degenerate olefin metathesis (Burdett *et al.*, 2004). This problem may be circumvented by performing cross-metathesis with a symmetrical internal olefin, such as 2-butene. Using second-generation Grubbs' catalysts, effective turnover numbers of up to 440,000 were found (Patel *et al.*, 2005). However, the catalyst efficiency was strongly dependent on the purity of both the methyl oleate and the 2-butene. The presence of polyunsaturates, or of 1,3-butadiene, leads to catalyst deactivation, likely *via* the formation of vinyl alkylidenes (Schwab *et al.*, 1996). In addition, the instability of the ruthenium methylidene intermediate in the ethenolysis pathway restricts reactions to low temperatures and, consequently, low rates. This limitation has been overcome to some extent with new Phoban-based Grubbs' catalysts, which show higher methylidene stability (Forman *et al.*, 2004).

Recently, the ethenolysis problem was tackled by simple substitution of the solvent system. Immobilization of a homogeneous catalyst in the liquid phase was achieved using an ionic liquid as solvent (Lacombe *et al.*, 2006). Under these conditions, the terminal α-olefins are only slightly miscible, and therefore separate spontaneously. This prevents the catalyst from being tied up in unproductive degenerate metathesis reactions, since it remains in the ionic liquid. High conversions can therefore be achieved, and the catalyst can be recycled and reused. However, the ecotoxicity of ionic liquids may be a concern (Wells and Coombe, 2006). Thus the search for effective, regenerable heterogeneous metathesis catalysts for converting FAMEs to other usable chemical feedstocks continues.

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TRANSFORMACIÓN CATALÍTICA DE LOS DERIVADOS DEL ACEITE A TRAVÉS DE METÁTESIS OLEFÍNICA

RESUMEN

Los estros de los ácidos grasos no saturados obtenidos del aceite vegetal, pasan por metátesis del vínculo C=C, con lo cual se forman nuevas olefinas internas y terminales, interesantes para la industria química. El factor clave en la realización de esta posibilidad industrial, es la posibilidad de sintetizarse los catalizadores correspondientes que puedan tolerar la presencia de diferentes grupos funcionales, guardando la reactividad hacia el vínculo olefínico interno, hasta en la ocasión de múltiple conversión. Los recientes perfeccionamientos de catalizadores y reactores, acercan estas metas a la realidad comercial.

TRANSFORMATION CATALYTIQUE DES DÉRIVÉS DE L'HUILE PAR LA MÉTATHÈSE D'OLÉFINES

RÉSUMÉ

Les esters d'acides gras non saturés obtenus de l'huile végétale passent par métathèse au lien C=C et de nouvelles oléfines internes et terminales intéressantes pour l'industrie chimique sont formées. Le facteur clef dans la réalisation de cette perspective industrielle est la capacité de synthétiser les catalyseurs qui seraient en mesure de tolérer la présence de différents groupes fonctionnels tout en gardant la réactivité envers le lien d'oléfine interne, et

même à haute conversion. De récents progrès dans les catalyseurs et les réacteurs rapprochent ces buts de la réalité commerciale.