Re-Based Heterogeneous Catalysts for Olefin Metathesis Prepared by Surface Organometallic Chemistry: Reactivity and Selectivity

Mathieu Chabanas, Christophe Copéret,* and Jean-Marie Basset*[a]

Abstract: Herein we describe the catalytic activity of **1**, a well-defined Re alkylidene complex supported silica, in the reaction of olefin metathesis. This system is highly active for terminal and internal olefins with initial rates up to 0.7 mol per mol Re per s. It also catalyses the self-metathesis of methyl oleate (MO) without the need of co-catalysts. The turnover numbers can reach up to 900 for MO, which is unprecedented for a heterogeneous Re-based catalyst. Moreover the use of silica as a support can bring major advantages, such as the possibility to use branched olefins like isobutene, which are usually incompatible with alumina-based supports; therefore, the formation of isoamylene from the cross-metathesis of propene and isobutene can be performed. All these results are in sharp contrast to what has been found for other silica- or alumina-supported rhenium oxide systems, which are either completely inactive (silica system) or typically need co-catalysts when functionalised olefins are used. Finally the initiation step corresponds to a cross-metathesis reaction to give a 3:1 mixture of 3,3-dimethylbutene and *trans*-4,4-dimethylpent-2-ene, and make this catalyst the first generation of well-defined Re-based heterogeneous catalysts.

Keywords: functionalized olefins · heterogeneous catalysis · metathesis · rhenium · silica

Introduction

Olefin metathesis was discovered more than 30 years ago by investigating the reactivity of olefin/alkane mixtures on Mo heterogeneous catalysts.[1, 2] The mechanistic understanding was a matter of a long debate in the chemical community of homogeneous catalysis and organometallic chemistry. The carbene mechanism initially proposed by Chauvin is now well accepted.[3] This mechanism gave rise to a tremendous effort in generating well-defined metallocarbenes of the Fischer and later Schrock types;[4] these were found to be highly active on their own. They have recently become more and more tolerant to functional groups and are now compatible with the needs of organic synthesis.[5] Although heterogeneous metathesis catalysts have been used commercially at a much larger scale than their homogeneous analogues (see, for example, the SHOP or the Phillips processes), little improvement has been achieved in their synthesis and performance. Even though the extremely active Re_2O_7/Al_2O_3 system was discovered in 1965, it is not yet used commercially to our knowledge.[6] This system has the advantage of working at moderate temperature, and can be compatible with functional groups when activated with organotin agents,[7] while Mo- or W-based heterogeneous catalysts typically work at relatively high temperatures (250–400 °C) and are usually not compatible with functionalised olefins.[2] One of the reasons for the difficulty of improving this interesting system is the very small number of active sites (typically less than 2 %);[8] this makes it difficult to obtain the structure–activity relationship.[9] All these parameters taken together probably explain why it has been so difficult to improve this system at least if one compares this heterogeneous catalyst with its homogeneous competitors. Therefore, it would be highly desirable to generate, on a surface, "single-site" Re-based catalysts that can be understood at a molecular level and thereby be improved by a rational approach.

We and others have been developing a series of well-defined single-site heterogeneous catalysts for various applications in catalysis, by using the concepts and tools of surface organometallic chemistry.[10] By this kind of approach, one designs and constructs the active site on a surface by attaching the metal centre to the oxide surface through a covalent (or ionic, or both) bond(s); these metal centres will have the necessary ligands to achieve the desired catalytic reaction. When applied to olefin metathesis the active site should be attached to the surface of a support through at least a covalent bond and contain a metallocarbene moiety in order to enter directly in the catalytic cycle (simple initiation step).

After considering various existing olefin metathesis catalysts developed both in homogenous and heterogeneous

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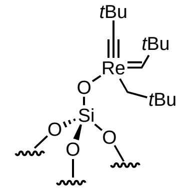
catalysis,[2] we have recently developed a well-defined rhenium–carbene surface complex **1**, [(≡SiO)-Re(≡C*t*Bu)(=CH*t*Bu)(CH$_2$*t*Bu)] supported on silica, that has been fully characterised.[11] Herein we would like to discuss its unprecedented reactivity in olefin metathesis and compared it with its classical heterogeneous catalyst competitors.

Results and Discussion



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Bringing propene (500 equiv) into contact with **1** in a batch reactor produces a thermodynamic mixture within two hours with an initial rate of 0.25 mol per mol Re per s, which is somewhat higher than that reported for Re-based heterogeneous catalysts supported on alumina (Figure 1a). The activity is higher by a factor of about 10^3 than that observed with classical silica supported Re catalysts.[12] Note that the *E*/*Z* ratio at low conversions in but-2-enes is neither the thermodynamic ratio (3:1) nor the statistical one (1:1), and probably corresponds to the true selectivity of the catalyst (2.5:1, Figure 1b). If the relative stability of the metallacyclobutane intermediates determines the stereochemical outcome of the reaction, the formation of *trans* but-2-ene is favoured by minimising 1,2-interactions in the corresponding metallacyclobutane intermediate: equatorial–equatorial (*e*,*e*) interactions (formation of the *trans* product) versus equatorial–axial (*e*,*a*) interactions (formation of the *cis* product).[13] During this reaction, neopentyl-containing products, namely 3,3-dimethylbutene and 4,4-dimethylpent-2-ene, also appear as an 1:3 mixture; this ratio is also compatible with the relative stability of the possible metallacyclobutane intermediates (Scheme 1), that is, by avoiding 1,2-interactions and minimising 1,3-interactions. These products arise from the initiation step, which is clearly a cross-metathesis. Note that for classical heterogeneous catalysts this initiation step is often difficult to understand, and for the Re$_2$O$_7$/Al$_2$0$_3$ system it is still a matter of debate.

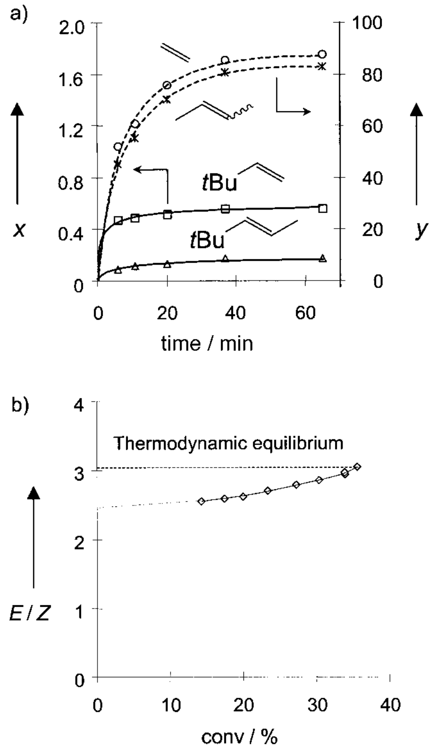
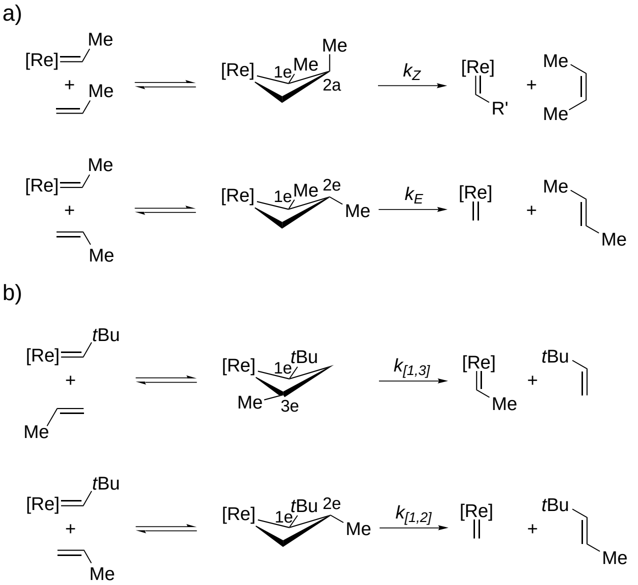


Figure 1. a) Propene metathesis (500 equiv) catalysed by **1** (1 equiv) at 25 °C. Evolution of products as a function of time. x = cross-metathesis products (3,3-dimethylbutene and (*E*)-4,4-dimethylpent-2-ene) in mol products per mol Re. y = propene metathesis products in mol product per mol Re. b) *E*/*Z* ratio in the formation of but-2-enes as a function of conversion of propene.



Scheme 1. a) Selectivity in metathesis of terminal olefins governed by 1,2-interactions in the rhenacyclobutane intermediate. b) Selectivity in initiation products (cross-metathesis with propene).

Additionally, *cis*-hept-3-ene (1000 equiv) as 1.2 M solution in dichlorobenzene is equilibrated in 8 h at 25 °C into a 1:1 mixture of hex-3-enes and oct-4-enes with an initial rate of 0.7 mol per mol Re per s (Figure 2). It is worth noting that the *E*/*Z* ratios for hex-3-enes and oct-4-enes are 0.75 and 0.6, respectively, and are constant up to 45 % conversion. Then the thermodynamic equilibrium is reached as conversion proceeds (7:1 *E*/*Z* ratio). This partial retention of configuration can also be related to the relative stability of the metallacyclobutane intermediates, which is governed by the minimisation of 1,3-interactions (Scheme 2).[13] Moreover these constant *E*/*Z* ratios show that hex-3-enes and oct-4-enes are the primary products over a large conversion for this system.

This catalyst can also achieve the self-metathesis of isobutene to 2,3-dimethylbut-2-ene, albeit with a slow rate (10^{-4} mol per mol Re per s). Interestingly, both initiation products, 3,3-dimethylbutene (R′ = *t*Bu; R = H) and 2,4,4-trimethylpent-2-ene (R′ = *t*Bu; R = CH$_3$), are obtained in a 1:3 ratio in agreement with the easier formation of a methylene rather than an isopropylidene carbene intermediate (Scheme 3). While this reaction is highly endothermic

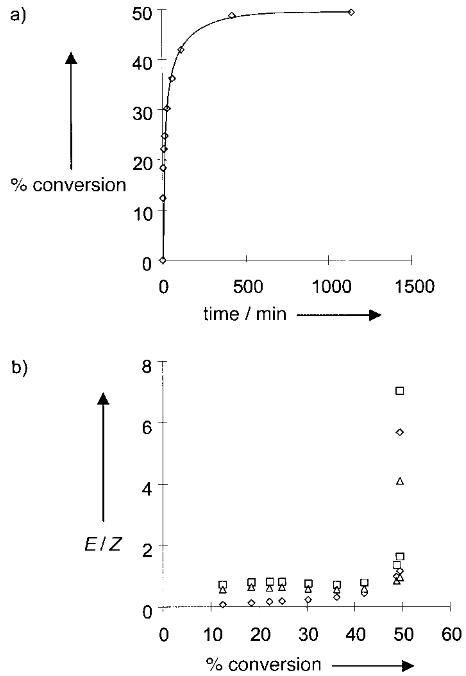
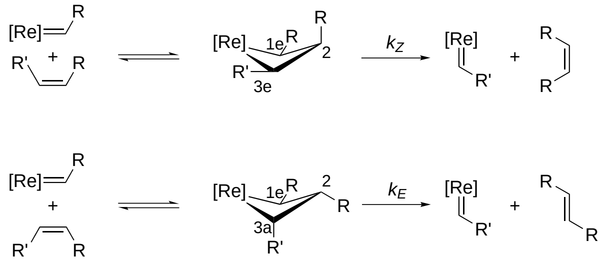


Figure 2. (*Z*)-Hept-3-ene metathesis (1000 equiv) catalysed by **1**. a) Conversion versus time. b) *E*/*Z* ratio versus conversion.



Scheme 2. Selectivity in metathesis of a *Z* olefin governed by 1,3-interactions of the rhenacyclobutane intermediate.

(17.3 kJ mol^{-1}), the cross-metathesis of propene and isobutene is more favoured (7 kJ mol^{-1}). Therefore upon contact of isobutene (500 equiv) and propene (500 equiv) with **1** at 25 °C two parallel reactions are observed: the self-metathesis of propene and the cross-metathesis of propene and isobutene; these reactions lead to an equilibrated mixture of ethylene (10%), propylene (29%), but-2-enes (4.5% as a 3:1 *E*/*Z* mixtures), isobutene (51%) and 2-methylpent-2-ene (3.5%), the cross-metathesis product of propene and isobutene. Note that isobutene does not give clean reactions on classical Re_2O_7/Al_2O_3 catalyst due to cationic-promoted side reactions (oligomerisation of isobutene).[14]

These promising results led us to investigate the reactivity of **1** towards functionalised olefins. Therefore the metathesis reaction of methyl oleate, a typical test substrate in heterogeneous catalysis, was attempted (Figure 3). When 100 equivalents of methyl oleate, as a 0.12 M solution in dichlorobenzene, was brought into contact with **1** at 25 °C, the thermodynamic equilibrium was reached within 1 h to give a 1:1 mixture of 9-octadecenes and dimethyl 9-octadecendioates [Eq. (1)]. The use of toluene or pentane as solvents provided similar results (Table 1). Noteworthy is the use of THF, which still allows the reaction to take place, albeit with a much slower rate. The solvent also has an influence on the selectivity: THF and toluene, for example, give the highest selectivity in the *Z* isomer (retention of configuration). Moreover when 2000 equiv of methyl oleate (1.2 M solution in toluene) are brought into contact with **1**, the

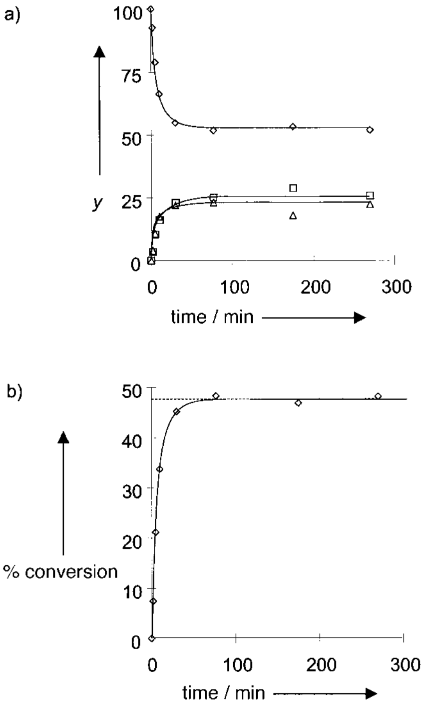
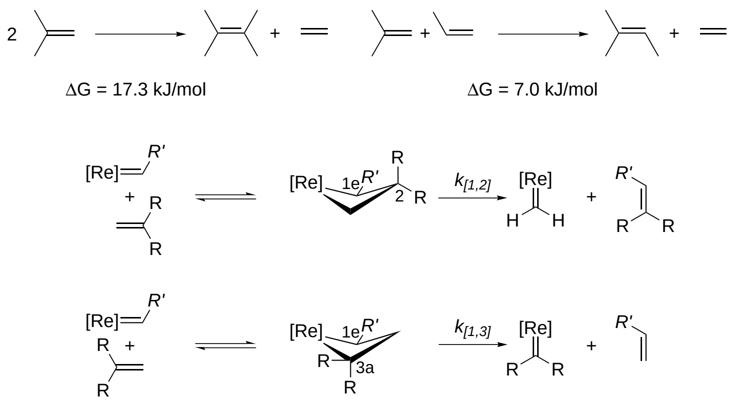
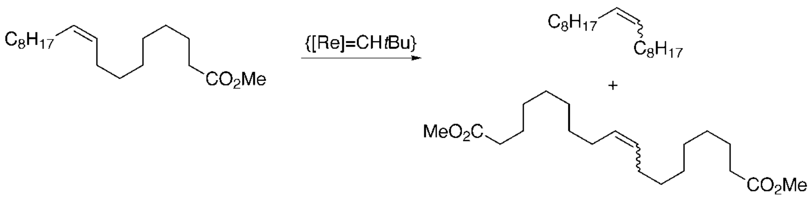


Figure 3. Methyl oleate metathesis (100 equiv) catalysed by **1**. a) Product formation [mol product per mol Re] (*y*) versus time. b) Conversion versus time.



Scheme 3. Self- and cross-metathesis reaction with isobutene. Selectivity in the metathesis of isobutene.



(1)

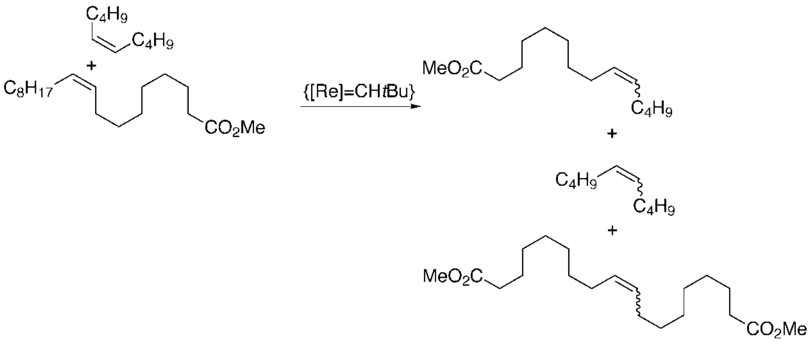
Table 1. Self-metathesis of methyl oleate catalysed by **1**, [(≡SiO)Re(CH$_2t$Bu)(=CHtBu)(≡CtBu)], at 25 °C. Initial turn-over frequencies and initial diastereoselectivities in various solvents.[a]

Solvent	Initial TOF [s^{-1}] (TON)	$(E/Z)_0$ ratio[b]
THF	< 0.002 (18)[c]	0.05–0.2
o-dichlorobenzene	0.07 (50)[d]	0.6–0.7
toluene	0.08 (50)[d]	0.2–0.4
octane	0.11 (50)[d]	0.6–0.9

[a] Experimental conditions: A 0.12 M solution (100 equiv) was brought into contact with **1** at 25 °C and analysed over time. [b] Selectivity at low conversions. [c] The reaction was stopped at 18 TON. [d] Equilibrium was reached.

thermodynamic equilibrium is almost reached, and a turnover number of 900 (TON) is obtained. Note that classical heterogeneous catalysts supported on alumina (or silica–alumina) even when activated by tin reagents typically give 25–160 TON.[2, 7, 15] Note also that no system supported on silica has been reported for the conversion of methyl oleate, while the closest homogeneous catalyst analogue [{R$_{F6}$O}$_2$-Re(=CHtBu)(≡CtBu)] reaches 25 TON.[16]

With this system, it is also possible to carry out cross-metathesis reactions. For instance, a 2:1 ratio of *trans*-5-decene (200 equiv) and methyl oleate (100 equiv) was converted within 3 h to the thermodynamic equilibrium (80 % conversion) and with a 80 % selectivity in the cross-metathesis product [Eq. (2)].



(2)

Conclusion

We have shown that the well-defined Re–carbene supported on silica is a highly active olefin metathesis catalyst even for functionalised olefins. Moreover this surface complex **1** readily converts ester-containing olefins without the need for a co-catalyst(s); this is a challenge that has been difficult so far for both homogenous and heterogeneous Re-based catalysts. The recent improvements of the Ru-based systems have been outstanding,[5, 17] and this well-defined Re-based system supported on silica is probably a first step towards the rational development of highly active and functional group compatible heterogeneous catalysts by a molecular approach of the construction of the active site.

Experimental Section

General procedure: The silica-supported complex **1** was prepared by using the literature procedure.[11] All catalytic tests were carried out under an inert atmosphere either using standard Schlenk techniques (gaseous reactants) or a glove-box (liquid reactants). Gaseous reactants, that is propene (Air Liquide), isobutene (Air Liquide), were dried over freshly regenerated molecular sieves (3 Å) and BTS traps (Fluka) before addition. (*Z*)-3-Heptene (96 %, Aldrich) was distilled under Ar over CaH$_2$. (*E*)-5-Decene (99 %, Aldrich) was degassed with four freeze–pump–thaw cycles, and dried over freshly activated molecular sieves (3 Å). Methyl oleate (99 %, Aldrich) was used as received unless otherwise specified. THF was distilled under N$_2$ over Na/benzophenone before use. *o*-Dichlorobenzene and toluene were distilled and stored over molecular sieves (3 Å). Octane was distilled and stored over Na. Octadecane (99 %, Aldrich) was used as received. GC analysis of light alkenes or alkanes (C$_1$–C$_9$) were performed on a gas chromatograph HP5890, equipped with a flame ionisation detector (FID) and a KCl/Al$_2$O$_3$ on fused silica column (50 m × 0.32 mm). Products of methyl oleate self- or cross-metathesis were analysed by using either a HP6890 apparatus (HP-1 column, 30 m × 0.32 mm) or a HP5890 apparatus (HP-5 column).

Metathesis of propene catalysed by 1: The complex **1** (20.4 μmol, 80 mg, 4.75 % wt Re) was introduced under Ar in a 381 mL batch reactor. After evacuation of the gas phase, propene ($P = 666$ hPa, 10 mmol) was added. During the reaction at 25 °C, aliquots were expended in a small volume, brought to atmospheric pressure and analysed by GC (see Figure 1).

Metathesis of (Z)-hept-3-ene catalysed by 1: A 1.23 M solution of (*Z*)-hept-3-ene in *o*-dichlorobenzene, containing heptane as internal standard, was prepared and dried over freshly activated molecular sieves (3 Å). The surface complex **1** (20 mg, 4 % wt Re, 4.3 μmol) was placed in a 5 mL batch reactor equipped with a conical magnetic stirring bar. The reactor was closed with a cap equipped with a Teflon septum. At $t = 0$, the (*Z*)-hept-3-ene solution (3.5 mL, 4.3 mmol) was added at 25 °C under vigorous stirring by syringe through the septum. During the reaction at 25 °C, aliquots (1–2 drops) were taken, diluted in pure *o*-dichlorobenzene (0.2 mL) and analysed by GC (see Figure 2).

Metathesis of isobutene catalysed by 1: The surface complex **1** (80 mg, 4.75 % wt Re, 20.4 μmol) was introduced under Ar in a 381 mL batch reactor. After evacuation of the gas phase, isobutene ($P = 666$ hPa, 10 mmol) was added. During the reaction at 25 °C, aliquots were expended in a small volume, brought to atmospheric pressure and analysed by GC (see text).

Propene–isobutene cross-metathesis catalysed by 1: The surface complex **1** (40 mg, 4.75 % wt Re, 10.2 μmol) was introduced under Ar in a 381 mL batch reactor. After evacuation of the gas phase, isobutene ($P = 333$ hPa, 5.12 mmol) and propene ($P = 333$ hPa, 5.12 mmol) were added. During the reaction at 25 °C, aliquots were expended in a small volume, brought to atmospheric pressure and analysed by GC (see text).

General procedure for the metathesis of methyl oleate: A solution of known concentration of methyl oleate in a solvent that contained octadecane as an internal standard was prepared, degassed with four freeze–pump–thaw cycles and dried over freshly activated molecular sieves (3 Å). The surface complex **1** (4.3 μmol) was placed in a 5 mL batch reactor equipped with a magnetic stirring bar. The reactor was closed with a cap equipped with a Teflon septum. At $t = 0$, the methyl oleate solution (3.5 mL) was added at 25 °C under vigorous stirring by syringe through the septum. During the reaction at 25 °C, aliquots (1–2 drops) were taken, diluted in pure solvent (0.2 mL) and analysed by GC.

Metathesis of methyl oleate (100 equiv in *o*-dichlorobenzene): The general procedure was followed with 3.5 mL of a 0.123 M solution of methyl oleate in *o*-dichlorobenzene.

Metathesis of methyl oleate (100 equiv in THF) catalysed by 1: The general procedure was followed with 3.5 mL of a 0.123 M solution of methyl oleate in THF and **1** as catalyst.

Metathesis of methyl oleate (100 equiv in toluene) catalysed by 1: The general procedure was followed with 3.5 mL of a 0.123 M solution of methyl oleate in toluene and **1** as catalyst.

Metathesis of methyl oleate (100 equiv in octane) catalysed by 1: The general procedure was followed with 3.5 mL of a 0.123 M solution of methyl oleate in octane and **1** as catalyst.

Metathesis of methyl oleate (2000 equiv in toluene) catalysed by 1: The general procedure was followed with 3.5 mL of a 1.23 M solution of methyl oleate (see purification below) in toluene and **1**. However, the amount of catalyst was halved: 2.15 μmol Re (10 mg of **1**, 4 %wt) in place of 4.3 μmol. Purification of the methyl oleate was performed as follows: alumina (0.75 g) was dried 3 h in an oven at 140 °C and then dried at 25 °C under high vacuum for 2 h. Commercial methyl oleate (4.6 g) and pentane were added and the mixture was stirred at 25 °C for 20 min. The methyl oleate solution in pentane was then filtered through Celite. Pentane was evaporated in high vacuum leaving pure methyl oleate, which was used to prepared a 1.23 M methyl oleate solution in toluene: methyl oleate (3.64 g, 12.3 mmol), octadecane (0.423 g, 1.66 mmol) and completion with toluene to a total volume of 10.0 mL. This solution was degassed and dried over molecular sieves (3 Å).

Cross-metathesis of a methyl oleate/(*E*)-dec-5-ene mixture catalysed by 1: A 0.124 M solution of methyl oleate in toluene was prepared, degassed with four freeze–pump–thaw cycles, and dried over freshly activated molecular sieves (3 Å). The surface complex **1** (20 mg, $4\,\%_{wt}$ Re, 4.3 μmol) was placed in a 5 mL batch reactor and (*E*)-5-decene (170 μL, 8.97×10^{-4} mol) was added by a precision syringe. The reactor was then closed with a cap that had a Teflon septum and the methyl oleate solution (3.5 mL, $4.34\ 10^{-4}$ mol) was added at 25 °C under vigorous stirring ($t = 0$) by syringe through the septum. During the reaction at 25 °C, aliquots (1–2 drops) were taken, diluted in pure solvent (0.2 mL) and analysed by GC.

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