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β-H Transfer from the Metallacyclobutane: A Key Step in the Deactivation and Byproduct Formation for the Well-Defined Silica-Supported Rhenium Alkylidene Alkene Metathesis Catalyst

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Abstract: The surface complex [(≡SiO)Re(≡C*t*Bu)(=CH*t*Bu)(CH₂*t*Bu)] (**1**) is a highly efficient propene metathesis catalyst with high initial activities and a good productivity. However, it undergoes a fast deactivation process with time on stream, which is first order in active sites and ethene. Noteworthy, 1-butene and pentenes, unexpected products in the metathesis of propene, are formed as primary products, in large amount relative to Re (> >1 equiv/Re), showing that their formation is not associated with the formation of inactive species. DFT calculations on molecular model systems show that byproduct formation and deactivation start by a β-H transfer *trans* to the weak σ-donor ligand (siloxy) at the metallacyclobutane intermediate having a square-based pyramid geometry. This key step has an energy barrier slightly higher than that calculated for olefin metathesis. After β-H transfer, the most accessible pathway is the insertion of ethene in the Re—H bond. The resulting pentacoordinated trisperhydrocarbyl complex rearranges via either (1) α-H abstraction yielding the unexpected 1-butene byproduct and the regeneration of the catalyst or (2) β-H abstraction leading to degrafting. These deactivation and byproduct formation pathways are in full agreement with the experimental data.

Introduction

Alkene metathesis has become a major chemical process to form C—C bonds in both the basic chemical and the pharmaceutical industries.[1–4] While the latest development of well-defined homogeneous catalysts has made possible their use in organic synthesis and polymer chemistry, basic chemical processes still rely on classical heterogeneous catalysts based on transition metal oxide supported on oxide materials (MoO₃, WO₃, or Re₂O₇ supported on silica, alumina, or magnesia).[4,5] The increasing world demand for propene has raised the interest in metathesis, which allows its production through the cross-metathesis of ethene and 2-butenes. In fact, several operating units associated with crackers have just started to produce propene via this process.[4] It is therefore important to understand the formation of products and deactivation processes of heterogeneous catalysts in order to implement strategies to develop more robust catalysts or/and regeneration procedures. In particular, for Re₂O₇/Al₂O₃, neither the mode of initiation of the propagating carbene nor its mode of deactivation is understood despite recent advances.[6–9] One of the aims of surface organometallic chemistry (SOMC) is to develop well-defined heterogeneous catalysts by a molecular approach in order to improve them through structure–reactivity relationships. In this view, we have recently prepared and characterized a well-defined silica-supported Re alkylidene complex, [(≡SiO)Re(≡C*t*Bu)-(=CH*t*Bu)(CH₂*t*Bu)] (**1**), which exhibits much greater activities in batch reactors than the classical heterogeneous catalyst analogues.[10–13] In addition, it also performs the metathesis of

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(9) Salameh, A.; Copéret, C.; Basset, J.-M.; Bohm, V. P. W.; Roper, M. *Adv. Synth. Catal.* **2007**, *349*, 238–242.
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functionalized alkenes without the use of cocatalyst in contrast to Re_2O_7/Al_2O_3.[14]

Here, we have therefore studied in detail the activity, the stability, and the selectivity of **1** in the metathesis of propene by a combined experimental and theoretical approach, focusing on the understanding of deactivation processes and formation of byproducts. This has been undertaken by the following investigations: (1) effect of time on stream on activity and selectivity in a flow reactor to obtain information on the stability of the system (deactivation), (2) kinetic modeling of deactivation and monitoring the fate of **1** by IR and NMR spectroscopies, (3) effect of contact time (inverse space velocity) on product selectivities in order to evaluate the pathway of formation of products (primary vs secondary), (4) origin of formation of byproducts by monitoring the products resulting from the reactivity of **1** with ^{13}C dilabeled ethene, and (5) evaluation of possible reaction pathways for the deactivation of the catalyst and the formation of byproducts through DFT calculations.

Results and Discussion

Activities and Selectivities as a Function of Time on Stream. The conversion of propene as a function of time on stream has been studied in a continuous flow reactor at 30 °C (see Experimental Details for more information). With a flow of 92 mL/min, after a very high initial rate (>120 mol propene/mol Re/min), which allows propene to be nearly transformed into thermodynamic mixtures of propene, ethene, and butenes (ca. 30% conversion), a fast deactivation ensued (Figure 1a). After 30 min, the conversion dropped to about 10%, and deactivation was still observed, *albeit* at a slower rate (vide infra). Over 145 min, more than 6000 mol of propene per mol of Re was transformed. The major products obtained were ethene and a mixture of 2-butenes as expected in alkene metathesis (Scheme 1). The selectivities for ethene and 2-butenes were 49.5 and 48%, respectively (Figure 1b). Except for the first data point ($t = 2$ min), for which the *E/Z*-2-butene ratio (2.55) and the conversion (28%) were close to the thermodynamic equilibrium (thermodynamic ratio and calculated conversion at 30 °C are 2.84 and 36, respectively), their selectivity was constant (*E/Z* = 2.0) as a function of time on stream. This selectivity is in agreement with what has been observed in the literature for other d^0 systems; that is, terminal alkenes typically give the (*E*)-alkene as the major kinetic product. This is due to a minimization of steric interactions between the substituent of the carbene ligands and the substituent on the incoming alkene in the formation of the metallacyclobutane (Scheme 1a), that is, when they are *anti* to each other.[15] At higher conversions (early stage of the catalytic test), *Z/E* isomerization of 2-butenes takes place (via metathesis, Schemes 1c), and therefore the thermodynamic ratio of 2-butenes is reached (*E/Z* ratio = 2.85).

Under flow conditions, like in a batch reactor,[10,14] the initiation products, 3,3-dimethylbutene (*t*BuCH=CH₂) and (*E*)-4,4-dimethyl-2-pentene (*t*BuCH=CHCH₃), are also observed. The ratio of 3,3-dimethylbutene and (*E*)-4,4-dimethyl-2-pentene is typically around 1.8–2.0 (it varies slightly between experiments), and this selectivity can also be explained by using the
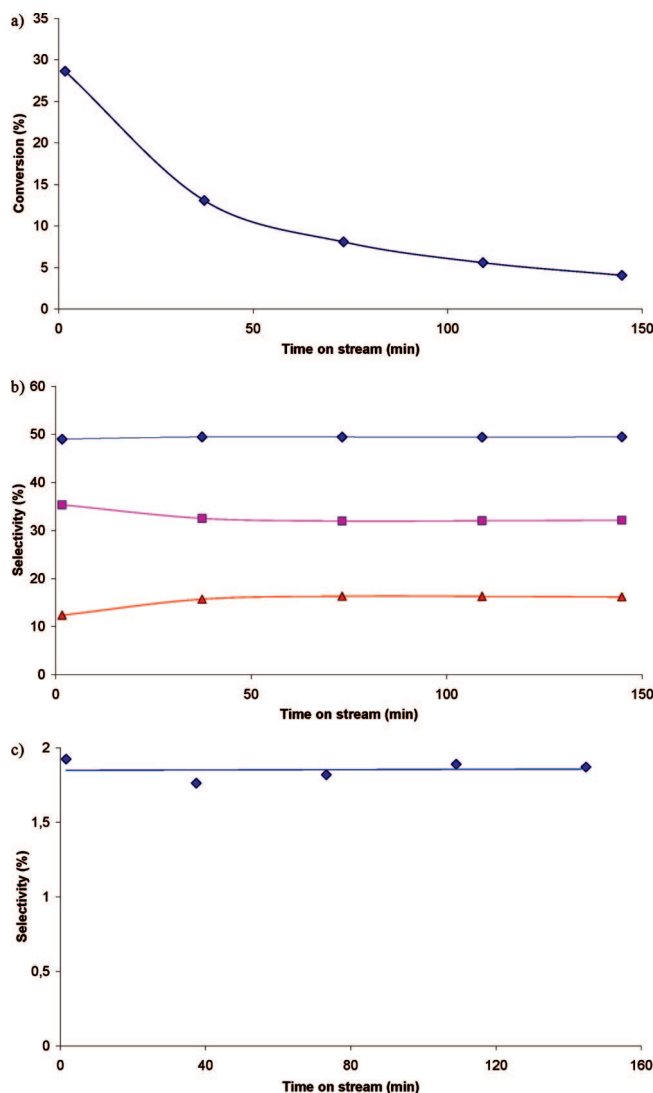
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Figure 1. (a) Conversion as a function of time on stream ($R = 411$ mol propene/mol Re/min, $F = 92$ mL/min). (b) Selectivities as a function of time on stream for the major products: (♦) ethene, (■) (*E*)-2-butene, and (▲) (*Z*)-2-butene). (c) Selectivities in 1-butene as a function of time on stream (for 2-methyl-2-propene, see Figure S1 and Table 1).

same model, involving the minimization of interactions between the incoming alkene, here propene (CH_2=$CHCH_3$), and the initiating metal–neopentylidene ligand, Re=CH*t*Bu (vide supra and Scheme 2). These initiation products are observed only during the first analysis (less than 20 min), which is consistent with a very fast initiation step and a well-defined active site precursor in contrast to classical heterogeneous catalysts for which the active sites are generated slowly during time on stream.[16,17] Additionally, 2,2-dimethylpropane is also detected as a minor products (0.2–1 equiv/3,3-dimethylbutene formed).

Moreover, besides the expected products of propene metathesis (ethene and 2-butenes), other unexpected alkenes [C₄ (1-butene and isobutene), C₅, and C₆ alkenes] (Figures 1c and S1) and alkanes (ethane and propane) are also formed. The selectivity in ethane and propane can only be evaluated at short time on stream (ca. 2 min) to ca. 0.03 and 0.23%, respectively. At

(16) Kapteijn, F.; Bredt, H. L. G.; Homburg, E.; Mol, J. C. *Ind. Eng. Chem., Prod. Res. Dev.* **1981**, *20*, 457–466.
(17) Chauvin, Y.; Commereuc, D. *J. Chem. Soc., Chem. Commun.* **1992**, 462–464.

Scheme 1[a]

a)

favoured

disfavoured

b)

c)

d)
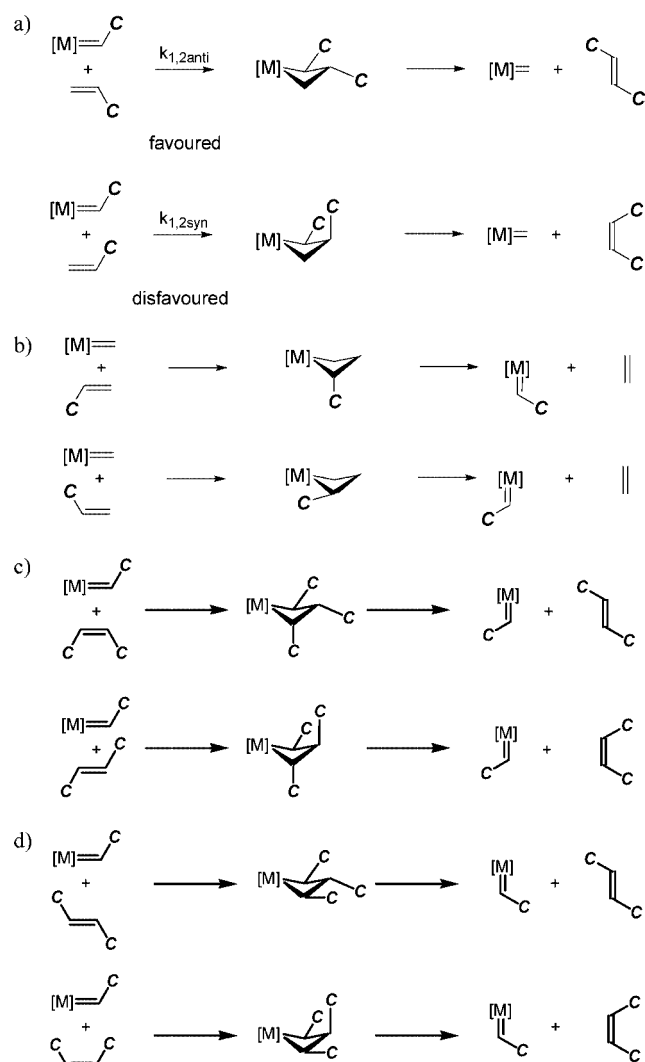
[a] Formation of (a) 2-butenes and (b) ethene, (c) *E/Z* isomerization of 2-butenes via alkene metathesis, and (d) fully degenerate metathesis.

Scheme 2. Mechanism for the Initiation Step

a) *favoured*

major

b) *favoured*

major

c) *disfavoured*
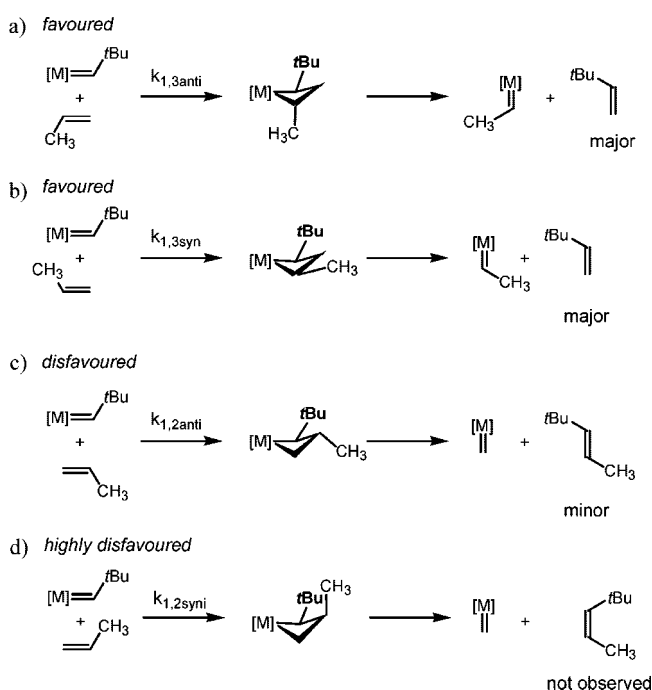
minor

d) *highly disfavoured*

not observed

Table 1. Selectivity When Inverse Space Velocity Tends toward Zero and Cumulated Amount of Products over 145 Minutes

product	selectivity (%)	cumulated amount (mol/mol of Re)
ethene	49.5	3260
(*E*)-2-butene	32.0	2195
(*Z*)-2-butene	16.0	984
1-butene	2.0	122
isobutene	0.001	0.5
(*E*)-2-pentene	0.13	29
(*Z*)-2-pentene	0.04	6.0
1-pentene	0.00	0.6
3-methyl-1-butene	0.03	1.0
2-methyl-1-butene	0.05	3.0
2-methyl-2-butene	0.06	5.0

longer time on stream, it is however difficult to quantify them with accuracy because it becomes increasingly difficult to measure their concentration in the feed as conversion decreases over time on stream and also because ethane and propane are present in the feed.

Notably, all C_4 and C_5 alkenes are present at all time (1-pentene only as traces), which shows that processes other than alkene metathesis are involved, possibly secondary reactions. The major byproduct (at 75 min) is 1-butene (1.9%) followed by 2-pentenes (0.3%), branched C_5 alkenes (0.15%) and 1-pentene (<0.01%).[18] The selectivities of byproducts at short time on stream (after ca. 2 min) are higher than after 45 min (except for 1-butene, 2-methyl-1-butene, and 3-methyl-1-butene). This phenomenon is probably due to the relatively high conversion (30%, close to the thermodynamic conversion, i.e., 35%), which favors secondary processes. Besides 6000 mol of propene per mol of Re converted within 145 min into ethene and 2-butenes, the metathesis products, more than 160 mol of byproducts per Re [1-butene (122/Re), isobutene (0.5/Re), and C_5 alkenes (42.5/Re)] is unexpectedly formed. Due to the large amount of 1-butene or other alkenes formed, their formation is not necessarily related to the formation of inactive species

because one would expect a 1:1 correlation between their formation and the amount of inactive Re species.

Deactivation. The deactivation of **1** in the metathesis of propene in a flow reactor is relatively fast and does not follow a simple first-order decay (eq 1) as expected for a loss of active sites through poisoning or intrinsic deactivation (Figure S2). This deactivation phenomenon is faster at higher than at lower conversions, and the deactivation model is greatly improved with a deactivation kinetic model being first order in active sites and products, ethene and/or 2-butenes (eq 2, Figure S2). The very good fit between the experimental and simulated loss of conversion as a function of time with this model shows that alkene products are involved in the deactivation process.[19] As deactivation is not related to propene (not first order) and probably to more substituted and less reactive alkenes such as 2-butenes, it is very likely that ethene is the main source of

(18) All alkenes could be observed and identified by GC and GC/MS, but the couples (*E*)-2-butene/1-butene and 1-pentene/2-methyl-1-butene could only be partially separated, which led to somewhat imprecise relative quantification of these products.

(19) Salameh, A.; Baudouin, A.; Soulivong, D.; Boehm, V.; Roeper, M.; Basset, J.-M.; Copéret, C. *J. Catal.* **2008**, *253*, 180–190.

Scheme 3. Reaction of [13]C Dilabeled Ethene on **1** (R = *t*Bu) and the Subsequent [13]C Labeled Methylidene Carbene Complex
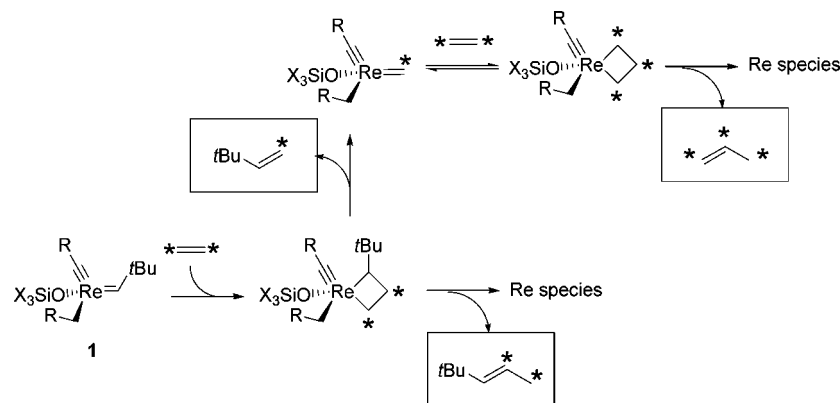
deactivation, as recently shown for MeReO₃/Al₂O₃ or Ru-based molecular catalysts.[19,20]

$$-\frac{d\text{cat}}{dt} = k[\text{cat}] \tag{1}$$

$$-\frac{d\text{cat}}{dt} = k[\text{cat}][=] + k'[\text{cat}] \tag{2}$$

where k is the rate constant of deactivation, [cat] is the concentration of active sites, and [=] is the concentration of ethene in the feed.

Moreover, monitoring the reaction over times by both IR and NMR spectroscopy indicates that perhydrocarbyl ligands disappear and that some OH groups are regenerated (Figures S3 and S4). This observation is consistent with the cleavage of the Re–O bond, which probably leads to inactive Re species. Note that some OH groups reappear as a broad signal, which is consistent with their interaction with adsorbed species. Overall, the data are consistent with a degrafting of the catalyst as metathesis occurs and as the catalyst deactivates.

Influence of Flow Rates (Inverse Space Velocity Studies) on Selectivities. In order to determine if a product is primary or secondary, its selectivity as a function of the inverse of the space velocity (also called contact time) has been studied. During these experiments, since a fast deactivation takes place during the catalytic test, corrections on conversions were applied to take into account deactivation (Table 1 and Figures S5–S8 in Supporting Information). After correction, conversion varies linearly with respect to the inverse space velocity, and therefore, propene metathesis is not limited by a mass transfer process under these conditions so that kinetic information can be obtained from the rates of product formation. Note that the conversion and the rate of transformation of propene are, respectively, 2.34% and 9.0 mol/mol Re/min after 285 min. Even after an important deactivation (≈10% of the initial activity), this catalyst is still more active than classical heterogeneous catalysts (9 vs 0.5 mol/mol Re/min for Re₂O₇/Al₂O₃ under the same experimental conditions).

When the inverse space velocity tends toward zero, the selectivity provides information on the product formation pathways (primary vs secondary products). Ethene selectivity is relatively constant (e.g., 49.5%) over a wide range of flow rates (Figures S5–S8). As expected from the Chauvin mecha-

nism,[21] ethene is a primary product. Yet, its selectivity decreases slightly from 49.5 to 49.0% for longer contact time, which suggests that it could be consumed via secondary processes (vide infra). The selectivity in (*E*)- and (*Z*)-2-butene is almost constant, as well; the *E/Z* ratio varies from 2.1 to 2.0 when the contact time decreases and is different from the thermodynamic ratio (*E/Z* = 2.85). When the inverse space velocity tends toward 0, the kinetic ratio is about 2.0, and it should be a characteristic of the active site of the catalyst. This stereoisomeric ratio is in fact fully consistent with what is expected for terminal alkenes (vide supra, Scheme 1).[15]

Noteworthy, the selectivity in 1-butene, a product unexpected from propene metathesis, is 1.8% and almost independent of inverse space velocity (Table 1). This is consistent with its formation through a primary process or a process much faster than alkene metathesis (vide infra for further discussion). Contrary to the selectivity in 1-butene, the selectivity in isobutene increases if the inverse space velocity increases but does not vanish to 0 when the inverse space velocity tends toward 0. It is not clear however whether isobutene is really a primary product or not because of the very low selectivity. Similarly, the selectivity of pentenes decreases when contact time decreases, but their selectivity does not vanish to 0, which is consistent with their formation through primary and secondary processes. Their formation through secondary processes probably occurs via the cross-metathesis of 1-butene and propene (eq 3). In the case of branched C₅ alkenes, the selectivity as a function of contact time is nearly constant, which is consistent with their formation through primary processes.

$$\tag{3}$$
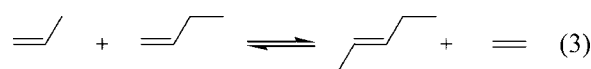
Origin of Products by Monitoring the Reaction of 1 with 1,2-[13]C Dilabeled Ethane. To further investigate the origin of byproducts, **1** was contacted with 13 equiv of 100% [13]C dilabeled ethene for 20 min. Besides the only expected product, that is, the monolabeled 1-^{13}C-3,3-dimethylbutene (0.4 equiv, > 95% [13]C monolabeled), resulting from the cross-metathesis of the neopentylidene and dilabeled ethene), alkene and alkane products are formed: ethane (0.2 equiv, >95% [13]C dilabeled), propene (4.1 equiv, >95% [13]C trilabeled), 1-butene (0.01 equiv, >90% [13]C tetralabeled), 2-butenes (0.25 equiv, >94% [13]C tetralabeled), isobutene (0.14 equiv, 85% [13]C tetralabeled), 2,2-dimethylpropane (0.34 equiv, unlabeled), and 1,2-[13]C₂-4,4-dimethyl-2-pentene (0.03 equiv, >95% [13]C dilabeled). The formation of these byproducts clearly indicates that several

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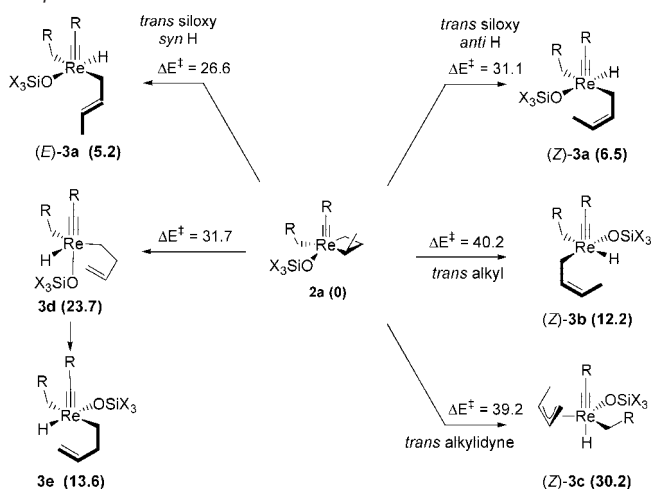
(21) Herisson, J. L.; Chauvin, Y. *Makromol. Chem.* **1971**, *141*, 161–176.

Scheme 4. Alkene Metathesis Reaction Pathway with **1**[a]
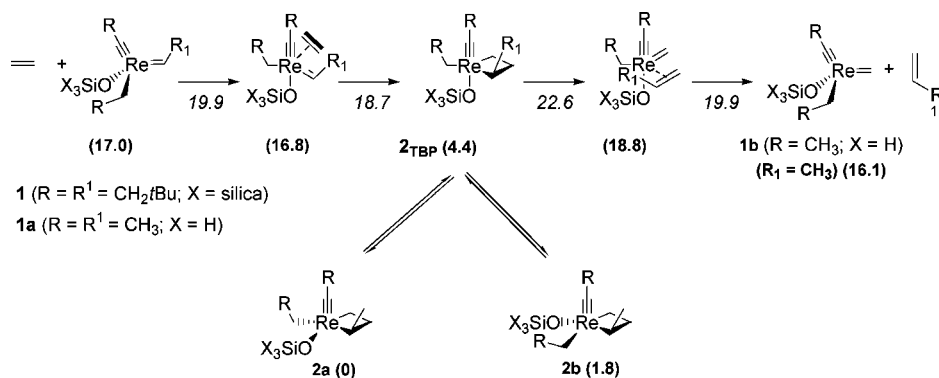
[a] The value in italics, below the arrow and in parentheses, corresponds to an energy barrier associated with the elementary step and the energies relative to **2a**, respectively (all energies in kcal mol^{-1}).

decomposition processes take place, and particularly, the formation of ^{13}C trilabeled propene and 1,2-$^{13}C_2$-4,4-dimethyl-2-pentene suggests that they originate from the decomposition of the metallacyclobutane intermediates (Scheme 3), and we have therefore further evaluated several decomposition pathways through DFT calculations.

Deactivation Pathways and Byproduct Formation from a DFT Study. DFT (B3PW91) calculations have been carried out to evaluate the preferred reaction pathways accounting for the formation of byproducts (1-butene, unexpected alkenes, and alkanes) and for a deactivation of the catalyst using Re(≡CCH_3)-(=CHCH_3)(CH_2CH_3)(OSiH_3) (*syn*-**1a**) as a model for **1**, where the *t*Bu groups have been replaced by methyls and the siloxy ligand of silica by OSiH_3. Similar modeling strategies have been successfully used to analyze the catalyst structures and the effect of ligands on initial activities and product stereochemistry.[13,22–33] Previous calculations have shown that alkene metathesis requires four elementary steps:[28,32] the initial coordination of the alkene to the d^0 metal center is followed by the [2 + 2]-cycloaddition to form a metallacyclobutane intermediate **2_TBP** with a TBP geometry, which is more stable than separated reactants (Scheme 4). This metallacyclobutane yields the products via [2 + 2]-cycloreversion and alkene decoordination but can also isomerize into more stable square-based pyramidal structures (SBP), which correspond to potential catalyst resting states. The most stable SBP metallacyclobutanes (diastereomers **2a** and **2b**) have the alkylidyne ligand at the apical position,[32] and interconversion between all metallacyclobutanes (TBP and all SBP)

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(32) Poater, A.; Solans-Monfort, X.; Clot, E.; Copéret, C.; Eisenstein, O. *J. Am. Chem. Soc.* **2007**, *129*, 8207–8216.
(33) Goumans, T. P. M.; Ehlers, A. W.; Lammertsma, K. *Organometallics* **2005**, *24*, 3200–3206.

Scheme 5. Decomposition of the SBP Metallacycle Intermediates via β-H Transfer[a]

[a] ΔE‡ is the energy barrier associated with the elementary step, and the values in parentheses are the energies relative to the reference compound **2a** (all energies are given in kcal mol^{-1}).
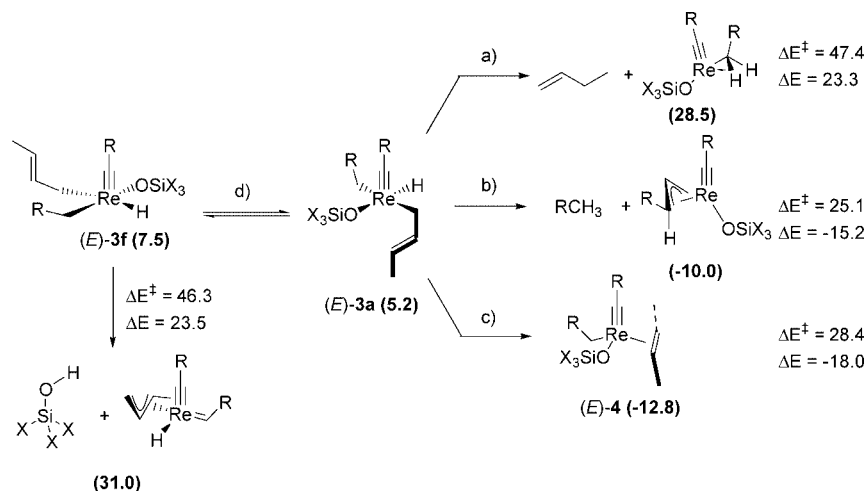
is possible as expected from the fluxional nature of pentacoordinated complexes.

Deactivation processes have been studied from the SBP metallacycle complex because it is the most stable intermediate on the potential energy surface and also because it has an empty coordination site, *trans* to the apical ligand. Cycloreversion from the metallacyclobutane intermediates **2**, yielding metathesis products, requires energy barriers of ca. 20–23 kcal mol^{-1}.[28,32] However, the presence of an empty coordination site in a SBP geometry allows other processes such as β-H transfer[34,35] and subsequent reactions. We have only considered the evolution of the most stable isomer **2a**, the processes starting from **2b** being very similar. In addition, deactivation pathways via dimerization are not described here because the surface species are isolated (on average by more than 10 Å) and also because their mobility is unlikely on highly dehydroxylated silica (no remaining OH groups).

The results are presented as follows: (1) Decomposition pathways of the SBP metallacycle intermediates through

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(35) Tobisch, S. *Organometallics* **2007**, *26*, 6529–6532.

Scheme 6. Decomposition of (*E*)-**3a** via Reductive Elimination Processes[a]

Scheme 7. Formation of Metallacyclopentane versus Re-formation of Alkyl–Alkylidene Complexes[a]
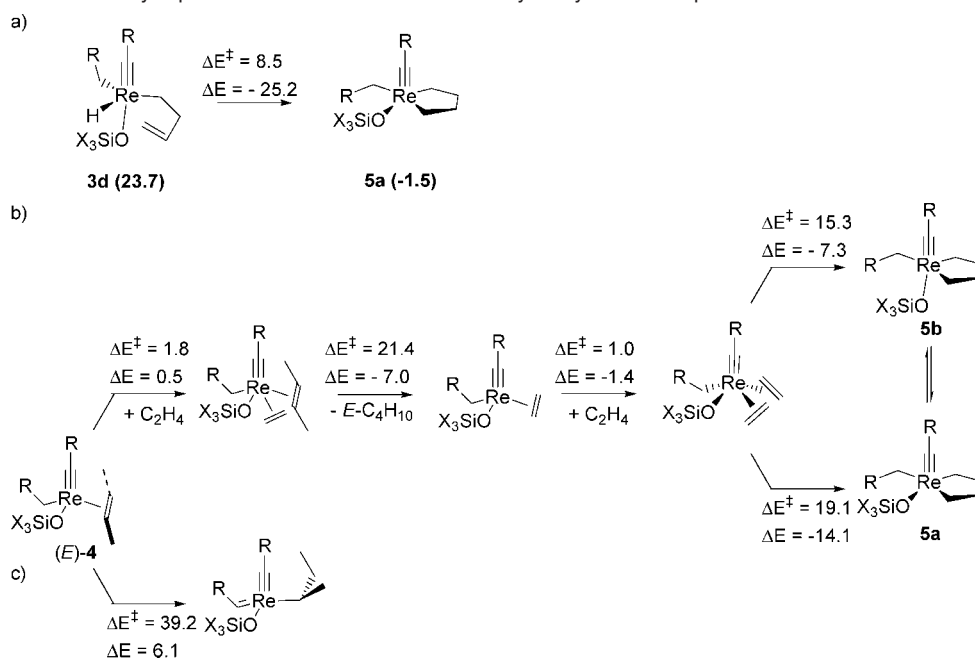
β-H transfer, generating a hydride complex, are discussed (Scheme 5).

(2) Transformations of the most accessible and most stable hydride species, (*E*)-**3a**, via reductive coupling processes (Scheme 6), metallacyclopentane formation (Scheme 7), and nonredox reactions (i.e., α-abstraction and alkene insertion processes) or H transfer processes (Scheme 8).

(3) The further decomposition of the most accessible intermediate (*E*)-**7**, resulting from insertion of ethene in the Re−H bond of (*E*)-**3a**, via α-H abstraction (Scheme 9) and β-H abstraction (Scheme 10). In order to compare competitive reaction pathways, all energy values in the schemes and in the Discussion are given relative to the most stable metallacyclobutane (**2a**) unless otherwise specified.

β-H Transfer from 2a. The β-H transfer can occur from the ring or the substituent leading to 2-butenyl and 3-butenyl complexes, respectively (Scheme 5). Even if the empty site is *trans* to the apical site of the SBP, the β-H transfer can occur *trans* to the alkylidyne, the alkyl, or the siloxy ligands (flexibility of pentacoordinated complexes). The β-H transfer from the ring preferentially occurs when the migrating hydride ligand is *trans* to the less σ-donating siloxy ligand (26.6 kcal mol^{-1}), leading to (*E*)- or (*Z*)-2-butenyl hydrido Re^{VII} complexes ((*E*)-**3a** and (*Z*)-**3a**). All processes involving a β-H transfer *trans* to either the alkyl (→**3b**) or the alkylidyne (→**3c**) ligands require much higher energy barriers (up to 40.2 kcal mol^{-1}). The most accessible β-H transfer (lower barrier) yields the most stable hydride complex ((*E*)-

Scheme 8. Decomposition of (*E*)-**3a** via (a) α-H Abstraction Processes, Migratory Insertion, or Insertion of an Alkene into the Re−H Bond or (b) Alkene Metathesis with a d² Complex*a*

a ΔE‡ and ΔE are the energy barrier and the reaction energy associated with the elementary step, respectively (all energies are given in kcal mol⁻¹, and the values in parentheses are the energies relative to the reference compound **2a**).
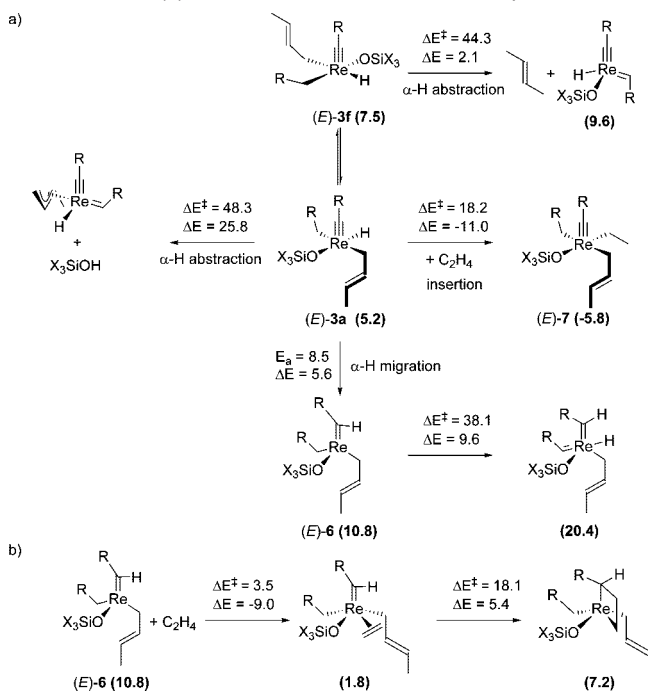
3a), which has a SBP geometry with an apical alkylidyne ligand, a (*E*)-2-butenyl ligand *trans* to the alkyl and the hydride *trans* to the siloxy ligand. The β-H transfer from the alkyl substituent requires a somewhat higher energy barrier compared to the formation of (*E*)-**3a** and yields a relatively high energy complex **3d**. The other β-H transfers have higher energy barriers and gives less stable intermediates than (*E*)-**3a** (Schemes 5 and S1), which shows that a ligand with poor σ-donating ability makes this process more accessible.

In the subsequent study, the reactivity of the more accessible and more stable (*E*)-2-butenyl hydrido intermediate is presented ((*E*)-**3a**, Schemes 6−10). Additional calculations, not discussed here, show that (*Z*)-**3a** follows similar energy profiles (Schemes S2−S5).

Reductive Coupling. Direct reductive coupling processes of two ligands from this pentacoordinated electron-deficient Reᵛᴵᴵ complex require relatively high energy barriers (Scheme 6). The two processes with accessible energy barriers (<30 kcal mol⁻¹) are (1) the reductive elimination of the hydride with the pending alkyl ligand (RCH₂, R = CH₃ in the calculated model or R = *t*Bu in **1**), leading to an alkane (RCH₃) and a π-allyl complex, or (2) the reductive coupling of the hydride and the (*E*)-2-butenyl ligand leading to a Reᵛ (*E*)-2-butene complex ((*E*)-**4**).

Formation of Metallacyclopentanes. From the intermediates **3** and **4**, stable metallacyclopentanes **5** can be obtained (Scheme 7). First, the metallacyclopentane **5a** is directly obtained by insertion of the double bond of the 3-butenyl ligand in the Re−H bond of **3d** with a low energy barrier (8.5 kcal mol⁻¹, Scheme 7a). Alternatively, a multistep process involving alkene exchange ((*E*)-2-butene by ethene) and oxidative coupling also yields

metallacyclopentanes (Scheme 7b). These two processes account for the formation of metallacyclopentanes (**5**), which has often been proposed and sometimes observed as a catalyst sink (not experimentally observed in the case of **1**).[36] Note also that the metallacyclopentane **5** is only marginally more stable than the SBP metallacyclobutanes (**2a,b**). Finally, note that (*E*)-**4**, an alkene complex, can be further transformed via α-H transfer from the alkyl ligand to the coordinated alkene into an alkyl–alkylidene complex, of structure and catalytic property similar to **1**, but with the loss of the original alkyl ligand (Scheme 7c).

Nonredox Reaction and H Transfers. Decomposition of (*E*)-**3a** and isomers via α-H abstraction requires significantly high energy barriers (>40 kcal mol⁻¹) and is therefore unlikely (Schemes 8a). In contrast, α-H transfer—migratory insertion of the hydride onto the alkylidyne in (*E*)-**3a**—generates an alkylidene Reᵛ complex ((*E*)-**6**) with a low energy barrier of 8.5 kcal mol⁻¹. Further α-H transfer from (*E*)-**6** to generate a bisalkylidene Reᵛᴵᴵ complex is energetically disfavored. On the other hand, this Reᵛ complex (*E*)-**6** can further react with ethene and re-enter a metathesis catalytic cycle (Scheme 8b), with energy barriers comparable with these of Reᵛᴵᴵ (Scheme 4). The metathesis pathway based on Reᵛ is associated with a stable alkene complex and a relatively unstable metallacycle, in contrast to what was obtained for Reᵛᴵᴵ, because of back-donation from Reᵛ. Finally, alkenes, especially ethene, can insert into the metal−hydride bond of (*E*)-**3a** to yield (*E*)-**7**, with a relatively low energy barrier of 18.2 kcal mol⁻¹ and a favorable reaction energy (Scheme 8a). This process is the most favored reaction occurring from (*E*)-**3a** because it associates low energy barriers with the formation of a thermodynamically favorable intermediate (*E*)-**7**.

Decomposition of (*E*)-7. All α-H abstraction processes (Scheme 9) have relatively low barriers (< ca. 30 kcal mol⁻¹) with the exception of the α-H abstraction by the siloxy ligand leading to a degrafting, which has a high energy barrier of 40.4 kcal mol⁻¹. This suggests that degrafting has to occur via a different pathway. The most favorable case corresponds to the transfer of a hydrogen from one of the alkyl ligands to the γ-allylic carbon of the 2-butenyl ligand (position 3, Scheme 9a), an exothermic process (−7.5 kcal mol⁻¹) associated with the lowest energy barrier of 23.4 kcal mol⁻¹. This process yields 1-butene, not expected from propene metathesis, and regenerates the catalyst (formation of a complex containing an alkyl, an alkylidene, an alkylidyne, and a siloxy ligand). This is consistent with the experimental observation of 1-butene being a primary product. Moreover, this process is not associated with deactivation but the regeneration of the catalyst, and this is also consistent with the formation of 1-butene in large amounts (>>1 equiv/Re, i.e., 122). Two comparable, *albeit* less favorable, processes (Scheme 9b,c) involve an α-H abstraction from the alkyl group (CH₂CH₃ or CH₂R) to other perhydrocarbyl groups, alkyl (CH₂CH₃/CH₂R) or 2-butenyl, which yields Reᵛᴵᴵ alkylidene complexes along with alkanes (ethane/CH₃R) or 2-butene, respectively. This is also consistent with the observation of alkanes during metathesis.

Of β-H abstraction processes (Scheme 10), only one of them is associated with a low energy barrier of 20.8 kcal mol⁻¹ (Scheme 10d); it corresponds to the β-H abstraction from an

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Scheme 9. Decomposition of (*E*)-**7** via (a) α′-H Abstraction by the 2-Butenyl Ligand, (b) α-H Abstraction by the 2-Butenyl Ligand, (c) α-H Abstraction by the Ethyl Ligand, and (d) α-H Abstraction by the Siloxy Ligand[a]
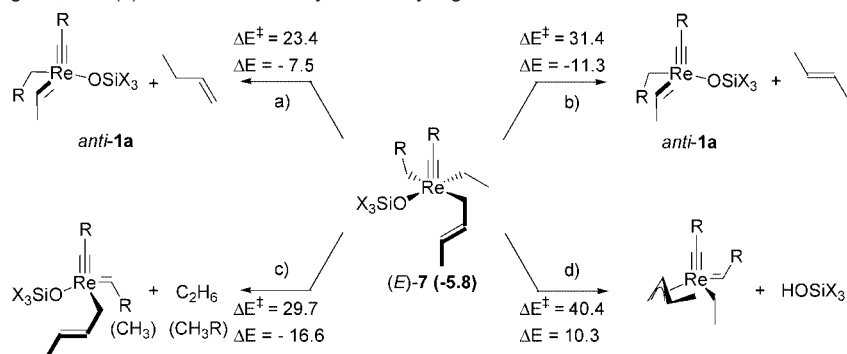
^{a} $\Delta E^{\ddagger}$ and ΔE are the energy barrier and the reaction energy associated with the elementary step, respectively (all energies are given in kcal mol^{-1}).

Scheme 10. Decomposition of (*E*)-**7** via (a) β′-H Abstraction by the 2-Butenyl Ligand, (b) β-H Abstraction by the 2-Butenyl Ligand, (c) β-H Abstraction by the Ethyl Ligand, and (d) β-H Abstraction by the Siloxy Ligand[a]
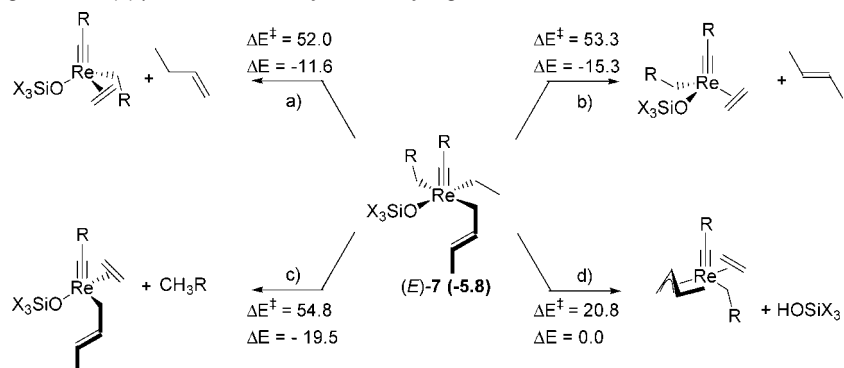
^{a} $\Delta E^{\ddagger}$ and ΔE are the energy barrier and the reaction energy associated with the elementary step, respectively (all energies are given in kcal mol^{-1}).

ethyl ligand by a siloxy ligand in a *cis* position. This yields a degrafted perhydrocarbyl complex and regenerates a silanol. This degrafting process requires one H in the β-position of the pending alkyl ligand. This hydrogen is not present in the original experimental catalyst, which has a neopentyl ligand (R = *t*Bu) but is introduced via insertion of ethene into the Re−H bond generated by decomposition of the metallacyclobutane through a β-H transfer.

Conclusion

The surface complex [(≡SiO)Re(≡C*t*Bu)(=CH*t*Bu)(CH₂*t*Bu)] (**1**) is a highly efficient propene metathesis catalyst with high initial turnover frequencies (>120 mol/mol/h) and good productivities (>6000 productive TON within 145 min). However, it undergoes a fast deactivation process with time on stream, which is first order in active sites and ethene. Noteworthy, 160 mol of byproducts/Re (1-butene and C₅ alkenes) is also formed in the first 145 min, hence their formation is not a priori directly associated with the formation of the inactive species. Moreover, their formation involves processes of rates similar (or greater) to this of alkene metathesis (formation of the thermodynamic amount of 1-butene), and they are apparently formed through primary processes, as evidenced by kinetic studies (no to low effect of the inverse space velocity on their selectivity).

DFT calculations show that the formation of byproducts and deactivation start by a β-H transfer at the SBP metallacyclobutane intermediates (e.g. **2a**) because of the presence of an empty coordination site for this geometry. The preferred reaction pathways associated with these processes are shown in Figure 2, with the energy profile for alkene metathesis being given for reference. The

β-H transfer step is associated with relatively low energy barriers of ca. 26–32 kcal mol^{-1}, slightly higher than the productive metathesis pathway (20–23 kcal mol^{-1}). After this critical β-H transfer step, several pathways with relatively low energy barriers can generate alkane byproducts as well as internal and terminal alkenes without deactivation of the catalyst (regeneration of a catalyst with ligands similar to these in **1**) as observed experimentally. The most accessible pathway following β-H transfer corresponds to the insertion of an alkene, ethene, into the Re−H bond. This yields a pentacoordinated trisperhydrocarbyl complex (**7**), which can rearrange through α-H and β-H abstraction processes. The α-H abstraction process is associated with the regeneration of the catalyst (formation of homologues of **1**) as well as the formation of alkenes and especially 1-butene. This is consistent with experimental data; 1-butene and pentenes are primary products not always associated with deactivation of the catalyst, and this also accounts for the formation of ^{13}C trilabeled propene and 1,2-^{13}C₂-4,4-dimethyl-2-pentene during the reaction of ^{13}C dilabeled ethene with **1** (Scheme 3). The β-H abstraction process always leads to deactivated species: (1) formation of alkene complex, which can yield metallacyclopentanes through oxidative coupling by reaction with another alkene, and (2) degrafting of the catalyst by abstraction of a β-H by a siloxy group. Note, however, that the latter cannot occur for the original catalyst **1** because of the absence of β-H in the original neopentyl ligands. In general, it has often been proposed that metallacyclopentanes correspond to a thermodynamic sink for alkene metathesis;[36] calculations show that SBP metallacyclopentanes are marginally more stable than the SBP metallacyclobutanes (only by ca. 2 kcal mol^{-1}). Re-forming metallacyclobutanes from metallacyclopentanes requires, however, high energy barriers of
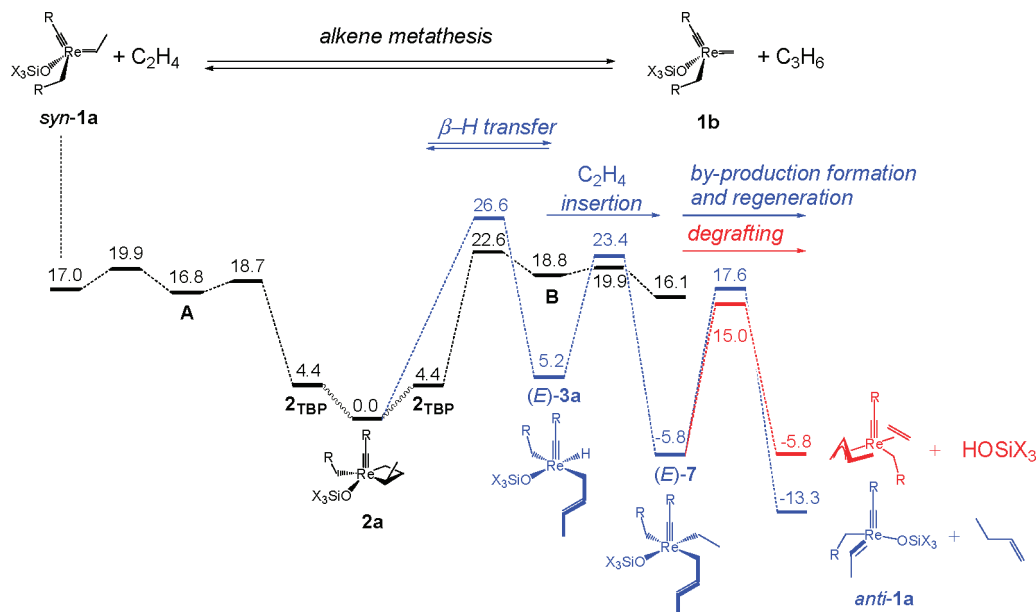
Figure 2. Energy profiles (kcal mol^{-1}) for alkene metathesis (black), formation of 1-butene with concomitant regeneration of the catalyst (blue), and deactivation via degrafting (red). The labels are given in Schemes 4−10.

ca. 30 kcal mol^{-1}, so that metallacyclopentanes are indeed not efficient reservoirs of active species. In the specific case of **1**, no experimental evidence for metallacyclopentane formation has been obtained, while degrafting has clearly been shown by IR and NMR spectroscopies; this process is therefore probably the major deactivation pathway. The involvement of an alkene, such as ethene, as a hydride scavenger leading to intermediates having β-H hence to the formation of inactive species is also consistent with experimental data: a first-order deactivation in ethene and active sites and a decrease of ethene selectivity at longer inverse space velocity (consumption of ethene). This study has been carried out for the well-defined silica-supported alkylidene rhenium surface complex, but in fact, the proposed deactivation pathways should apply to all d^0 tetracoordinated alkene metathesis catalysts whether supported or not,[37] even if, in the specific case of homogeneous catalysts, deactivation through dimerization has already been clearly identified. In conclusion, this approach has clearly helped to point out the processes involved in the byproduct formation and deactivation pathways, but further work would be needed, such as investigation of the systems with the whole ligands, if ones wants to quantitatively evaluate the actual relative rates of these various processes. The long-term aim is to provide a molecular understanding of deactivation processes for a variety of systems as a way to help the design of more efficient catalysts; this includes a study of the influence of the metal and ligands as well as the importance of dimerization processes, more relevant to nonsupported catalysts.[38]

Experimental Details

General Procedure. All experiments were carried out under controlled atmosphere, using Schlenk and glovebox techniques for the organometallic synthesis and loading of the catalyst. The catalyst **1**, [(≡SiO)Re(≡CtBu)(=CHtBu)(CH$_2t$Bu)], was prepared according to the literature procedure.[11] Elemental analyses were performed at the Service Central d'Analyses of CNRS in Solaize. Quality of the catalyst was controlled by ^{1}H MAS and ^{13}C CP-MAS solid state NMR spectroscopy, recorded on a Bruker DSX-300 or a

Bruker Avance-500 spectrometer at the Laboratoire de Chimie Organometallique de Surface in Ecole Supérieure de Chimie Physique Electronique de Lyon.

Reaction of (≡SiO)Re(≡CtBu)(=CHtBu)(CH$_2t$Bu) with Propene in the Continuous Flow Reactor. Propene was purchased from Scott (N35, purity 99.95%) and purified on custom-made traps by Sertronic (2 L). The flow rate was controlled and monitored by a mass-flow controller (Brooks). A pressure regulator controlled the inlet pressure. The reaction chamber was a cylindrical stainless-steel microreactor (diameter = 1 cm ; length = 18 cm), which could be filled in a glovebox. The volume could be varied by placing inserts (2 inserts, $L = 4$ cm, $V = 3.1$ cm^3; 1 insert, $L = 11$ cm, $V = 8.6$ cm^3; 0 insert, $L = 18$ cm, $V = 14.1$ cm^3). The pressure, the flows, and the temperature were monitored via West indicators/regulators. After release of the pressure (via a control pressure valve from Kammer), the gases were analyzed by gas chromatography (KCl/Al$_2$O$_3$).

For each reaction in the continuous flow reactor, the flow rates are controlled by a mass-flow controller (Brooks) and are in the range 20–100 mL/min. The catalyst was first loaded in the reaction chamber in a glovebox. The isolated reaction chamber was then connected with the reactor system, the tubes were flushed for 2 h, and the reaction chamber valve was opened ($t = 0$ for the catalytic test) so that propene could pass over the catalyst.

There was no accumulation of products on the catalyst since the variation of the total surface area never exceeded 2% and NMR spectroscopy of the resulting solid after the catalytic test did not show any peaks characteristic of oligomers. It was not possible to use propane (1% in propene) as an internal standard because some small amount of propane is formed along the catalytic test. The propene conversion and selectivity were therefore calculated as follows:

$$\text{conv} = \frac{\text{mol of propene transformed}}{\text{mol of propene (introduced)}}$$
$$\approx \frac{1 - \text{corrected surface area of propene}}{\sum \text{total corrected surface area}}$$

$$S_i = \frac{\text{mol of product i formed}}{\text{mol of propene converted}}$$
$$\approx \frac{\text{corrected surface area of product i formed}}{\sum \text{corrected surface area of products}}$$

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Simulation of Deactivation. Deactivation has been modeled by numerical simulation of the conversion of propene as a function time (A) based on A_0 (the initial conversion of propene, which is proportional to the number of active sites $\{A \propto [\text{cat}]$ in eqs 1 and 2$\}$ at $t = 0$ min), k (the rate constant of deactivation), and $[=]$, the concentration of ethene measured in the feed (/mol) (eq 4 and 5, Figure S2).

$$-\frac{\Delta A}{\Delta t} = k[A] \tag{4}$$

$$-\frac{\Delta A}{\Delta t} = [A] \times (k[=]\text{measured} + k') \tag{5}$$

Reaction of [($\equiv$SiO)Re($\equiv$C*t*Bu)(=CH*t*Bu)(CH$_2$*t*Bu)] (1) with ^{13}**C Dilabeled Ethane.** The catalyst [($\equiv$SiO)Re($\equiv$C*t*Bu)-(=CH*t*Bu)(CH$_2$*t*Bu)] (69 mg, 0.0074 mmol Re) was contacted with ^{13}C dilabeled ethene (13 equiv, 0.099 mmol, $P = 120$ hPa) in a 20 mL reactor. After 20 min, the gases were condensed for 1 h into another reactor kept at -196 °C and the resulting gases analysed by GC and GC/MS using KCl/Al$_2$O$_3$ column.

Computational Details. Calculations have been carried out with the hybrid B3PW91 density functional,[39,40] as implemented in the Gaussian03 package[41] on the model systems Re($\equiv$CCH$_3$)-(=CHCH$_3$)(CH$_2$CH$_3$)(OSiH$_3$) for **1a**. The Re and Si atoms have been represented with the quasi relativistic effective core pseudo-potentials (RECP) of the Stuttgart group, and the associated basis sets were augmented with a polarization function (Re: $\alpha = 0.869$; Si: $\alpha = 0.284$).[42,43] The remaining atoms (C, H, O) have been represented with 6–31G(d,p) basis sets.[44] The B3PW91 geometry optimizations were performed without any symmetry constraints, and the nature of the extrema (local minima or transition states) was checked by analytical frequency calculations. The discussion of the results is based on the electronic energies E without any ZPE corrections because inclusion of the ZPE corrections does not significantly modify the results. The free energy values G computed with Gaussian03 at 298 K and $P = 1$ atm are given in the Supporting Information. It was verified that considering free energies in place of E gives the same trends.

Supporting Information Available: Figures S1–S8, Schemes S1–S5, full list of authors for Gaussian03, list of Cartesian coordinates, energies E, free energies G of all calculated species. This material is available free of charge via the Internet at http://pubs.acs.org.

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