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Unprecedented Multifunctionality of Grubbs and Hoveyda–Grubbs Catalysts: Competitive Isomerization, Hydrogenation, Silylation and Metathesis Occurring in Solution and on Solid Phase

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Abstract: This contribution showcases the interplay of several non-metathetic reactions (isomerization, silylation and "hydrogen-free" reduction) with metathesis in systems comprising a functionalized olefin and a soluble or resin-immobilized silane. These competing, one-pot reactions occur under activation by second-generation Ru-alkylidene catalysts. Different olefinic substrates were used to study the influence of the substitution pattern on the reaction outcome. Emphasis is placed upon the rarely reported yet important transformations implying a solid phase-supported silane reagent. Catalytic species involved in and reaction pathways accounting for these concurrent processes are evidenced. An unexpected result of this research was the clearly proved partial binding of the olefin to the resin, thereby removing it from the reacting ensemble.

Keywords: cross-metathesis; reduction; silylation; isomerization; solid-phase; olefins; ruthenium catalyst

1. Introduction

Ruthenium metathesis catalysts have long been known to also promote, in homogeneous or heterogeneous phase, different chemical processes [1–3] such as olefin isomerization [4–8], hydrogenation [9], oxidation [10] and oxidative dehydrogenation [11], atom transfer radical addition [12,13], cyclization [14] and polymerization [15], cyclopropanation [16–19], cycloisomerization [20], etc. These mechanistically distinct reactions might compete with metathesis, even to a large extent, producing undesired secondary products, thus diminishing the efficiency of olefin metathesis. Various physical or chemicals methods have been implemented in order to suppress such problematic side reactions (notably isomerization). Thus, with the 2nd generation Grubbs catalyst (**1**), isomerization induced by in situ generated ruthenium-hydride complexes [4–8,21,22] is negatively influencing the yield and product selectivity, creating difficulties in product separation and purification. Olefin isomerization has been decreased by the addition of electron-deficient benzoquinones (e.g., 1,4-benzoquinones, 10 mol %), tricyclohexylphosphine oxide (0.5 mol %) or phenylphosphoric acid (5 mol %), as well as quinone-containing Hoveyda-type complexes [23–27]. Also proved was that for other 2nd generation Ru metathesis catalysts, the contribution of the isomerization pathway hinges on the catalyst loading [28].

Nevertheless, non-metathetic reactions initiated by ruthenium alkylidene catalysts can provide an expedient entry into otherwise inaccessible interesting compounds. In particular, isomerization and hydrogenation have industrial relevance being used to convert low-value coal- or petroleum-based by-products (e.g., lower alpha olefins) or olefins from renewable oil feedstocks into useful starting materials for the production of surfactants, detergents, lubricants, cosmetics, etc. [29].

Whereas the aforementioned homogeneous non-metathetic reactions with Grubbs catalysts are very well documented, occasionally even by the pairwise use of metathesis/non-metathesis protocols [30], there are some aspects about the competitive reactions that are still unclear. In heterogeneous phase, named solid-phase organic synthesis, we have carried out pioneering work on the application of a combination of ruthenium-catalyzed cross-metathesis and reduction to perform a formal alkane metathesis to build C*sp*^{3}–C*sp*^{3} linkages [31,32]. Solid-phase organic synthesis (SPOS), initially used in peptide chemistry, is now broadly applied to the preparation of a range of biologically interesting structures [33–35].

Apart from our work, very few studies have been published on heterogeneous non-metathetic reactions with Grubbs catalysts [36]; however, no report related to the use of solid-phase reagents has been disclosed so far. Utilization of reagents bound to a solid support has a number of advantages [37]: (i) alike traditional SPOS, purification is achieved by filtration; (ii) reactions can be monitored by standard organic techniques such as thin-layer chromatography since starting material and product are in solution phase; (iii) toxic, explosive or odorous reagents become safe after immobilization; and (iv), perhaps the most important present-day feature, solid-phase reagents are especially suitable for flow chemistry [38].

In this contribution, we delve into the different competing pathways for metathesis and non-metathesis reactions that happen during ruthenium-catalyzed double-bond reduction of functionalized olefins, under the action of triethylsilane or the unexplored solid-phase reagent, 4-(diethylsilylbutyl) polystyrene resin.

2. Results and Discussion

Reactions of mono- or disubstituted alkenes were carried out either homogeneously or with resin-supported silanes, in the presence of the Grubbs (**1**) or Hoveyda–Grubbs (**2**) initiators (Figure 1).

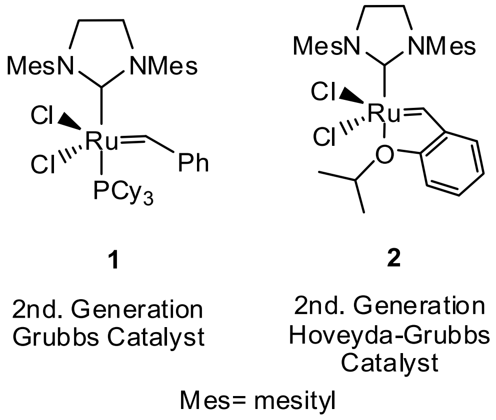
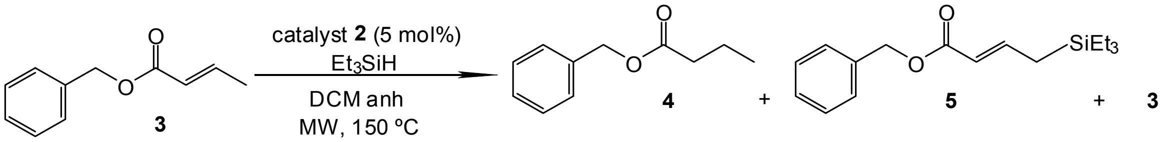


Figure 1. 2nd generation Grubbs and Hoveyda–Grubbs catalysts.

We first examined the reduction of *trans*-benzyl crotonate (**3**) with triethylsilane as reducing agent, in homogeneous phase, in presence of catalyst (**2**) and under microwave(MW)-enhanced heating. Detailed analysis of the crude product at different reaction times showed that, in most cases, some unreacted (**3**) was found, even for excess of silane (up to 5 equiv.). A summary of the study is shown in

Table 1. Along with the desired reduction product (**4**), an unexpected silylated compound, the benzyl (4-triethylsilyl)-*trans*-crotonate (**5**), was formed.

Table 1. Reduction of *trans*-benzyl crotonate (**3**) with triethylsilane catalyzed by **2** [a].



Entry	Et_3SiH (equiv.)	Products (3/4/5) [b]	
		Molar Ratio	Percentage (%)
1	0.5	10.5/1.0/1.4	81/8/11
2	1.0	4.4/1.0/0.4	76/17/7
3	2.5	0.9/1.0/0.3	41/46/13
4	5.0	0/1.0/0.1	0/91/9

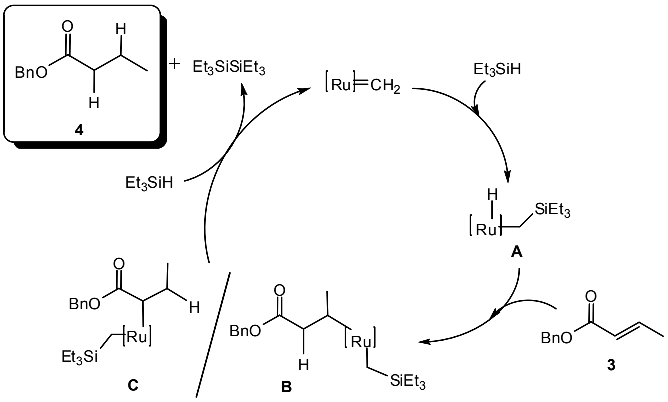
[a] Conditions: olefin **3**, Hoveyda–Grubbs catalyst (**2**; 5 mol %), microwave reactor (maximum power; 150 °C), reaction time 30 min, in anhydrous dichloromethane (DCM); [b] Determined from the ^{1}H-NMR (nuclear magnetic resonance) of the crude product.

At low concentration of triethylsilane (0.5 equiv., Entry 1) the allylsilane **5** overpassed **4** in the reaction output, whereas at higher concentrations of triethylsilane, the reduction compound **4** was predominant (Table 1, Entries 3 and 4). The underlying rationale is that the increased availability of the hydrogen source at high triethylsilane content raises the concentration of Ru hydride species responsible for the hydrogenation pathway, favouring reduction over hydrosilylation. Thus, an interplay between two non-metathetical reactions—reduction and isomerization—is unmasked in the present study. Intervention of isomerization was to be expected, especially because we operated at high temperature (150 °C) using the 2nd generation Grubbs catalyst known to be isomerization-prone. The reduction product **4** may arise either directly from **3** or from its isomerized counterpart **6** (vide infra).

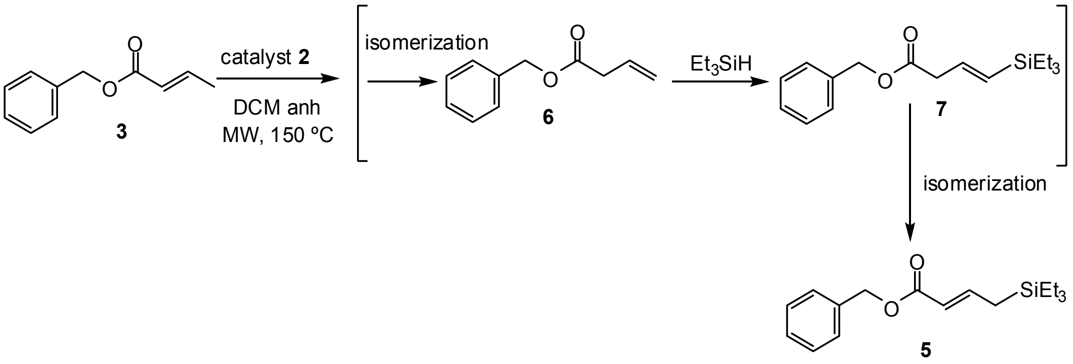
Interestingly, we have previously reported that, under conditions similar to Entry **4** but using the Grubbs catalyst (**1**), a nearly quantitative yield of **4** was obtained, without formation of any silylated compound [31].

Though olefin reduction with Et_3SiH activated by Grubbs carbenes is a well-known catalytic process, its mechanism is still not very clear [2,9,39,40]. Cossy et al. have proposed a mechanism that involves the addition of Et_3SiH to the Ru carbene to form an active Ru-hydride species (**A**) (Scheme 1) [9]. Then, species **A** would give **B** or **C** by insertion of **3** into the Ru–H bond. Lastly, **B** (or **C**) would suffer an elimination reaction regenerating the ruthenium carbene. In our case, hexaethyldisiloxane was detected in the final crude mixture. Formation of disiloxanes was also reported by Cossy et al. in the same publication [9]. Silanes have weak Si-H bonds and formation of hexaethyldisiloxane can be explained by an oxidation of Et_3SiH [41]. It is known that alkyldisiloxanes can be obtained by air oxidation from Et_3SiH in the presence of Lewis acids [42]. At the beginning, a radical pathway was considered, since formation of free radicals by changing oxidation state from +2 to +3 in some carbene-ruthenium complexes had been reported [43]. Nevertheless, reaction was unaffected by addition of a radical inhibitor such as di-*tert*-butyl nitroxide (DTBN), consequently a radical mechanism was ruled out.

Formation of the other reaction product, the silylated compound **5**, may occur through the following sequential steps: (i) isomerization of the internal olefin **3** into the terminal olefin **6**; (ii) direct silylation of the latter to the corresponding vinylsilane (**7**); (iii) finally, a second isomerization of **7** to the allylsilane **5** (Scheme 2).

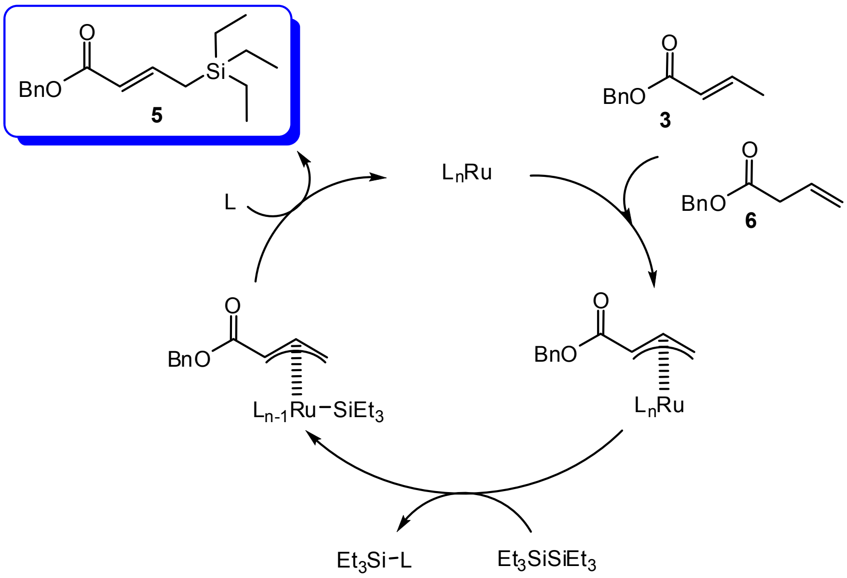


Scheme 1. Proposed mechanism for Et_3SiH-reduction of olefin **3** activated by catalysts **1** or **2**, according to Cossy et al. [9].



Scheme 2. Formation of the silylated derivative **5**.

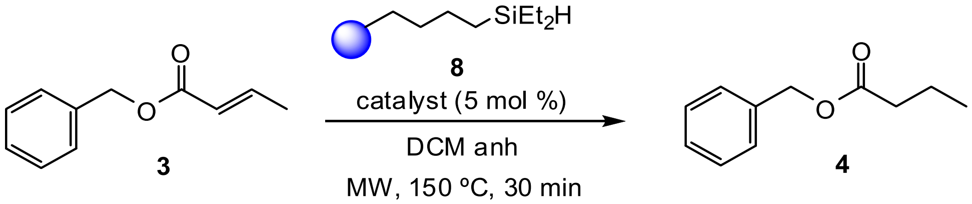
An allylic mechanism, by intermediacy of allyl-Ru complexes, might also be considered in the generation of **5** from the internal (**3**) and terminal olefin (**6**) when the disilane $Et_3SiSiEt_3$ would be present in the reacting system (Scheme 3).



Scheme 3. Possible allylic mechanism for the silylation of olefins **3** and **6** to the allylsilane **5**.

As mentioned in the Introduction, solid-phase reagents are gaining popularity in synthesis due to some comparative advantages especially useful for flow chemistry. Particularly, to the best of our knowledge, silanes immobilized on solid phase have not been applied to non-metathetic hydrogenations. Using high-loading Merrifield resin, we prepared 4-(diethylsilylbutyl) polystyrene resin (**8**) in two steps according to literature [44] (Table 2). Upon reacting benzyl *trans*-crotonate (**3**) with **8** in presence of catalyst **1** or **2**, a different outcome has been attained. Concerned are both the nature of the products and a more intricate pattern of the reactions routes, this time also involving metathesis (Table 2).

Table 2. Reduction of benzyl *trans*-crotonate (**3**) using resin-immobilized silane (**8**) or triethylsilane, in presence of catalyst **1** or **2**.



Entry	Olefin	Catalyst (5 mol %)	Silane (Equivalents)	Reaction Conditions [a]		Ratio 4:3 [b]
				Temp. (°C)	Time (h)	
1	**3**	**2**	**8** [c], 3.0	Reflux	24	1:19
2	**3**	**2**	**8** [c], 2.5	55 (sealed system)	16	1:5.6
3	**3**	**2**	**8** [c], 2.5	150 (MW) [d]	0.5	1:0.3 [e]
4	**3**	**2**	- [f]	150 (MW) [d]	0.5	1:0.3 [e]
5	**3**	**1**	**8** [c], 2.5	150 (MW) [d]	0.75	1:3.2 [e]
6	**3**	**2**	**8** [c], 0.75	150 (MW) [d]	0.5	ND [g]
7	Resin from Entry 6	**2**	Et_3SiH (2.5)	150 (MW) [d]	0.5	1:0.6 [h]

[a] In anhydrous dichloromethane; [b] Estimated from ^{1}H-NMR of the crude reaction mixture; [c] Synthesized resin, loading 2.8 mmol/g (theoretical loading calculated from the initial loading level of Merrifield resin (3.8 mmol/g)); [d] MW = microwave heating; [e] The ^{1}H-NMR spectrum of the crude reaction mixture showed a by-product, subsequently identified as **11** (see Supplementary Materials, Figures S15–S17); [f] The crude from Entry 3 was filtered and, after adding a supplementary amount of catalyst **2** (5 mol %), heating was repeated; [g] The product composition was not determined (ND), the filtered resin was used in a subsequent experiment (Entry 7; see also text); [h] The ^{1}H-NMR spectrum of the crude reaction mixture showed a by-product, identified by NMR techniques as **5** (see Scheme 1 and Supplementary Materials, Figures S1–S9).

Only low conversions to the reduced product **4** could be attained in refluxing dichloromethane, even at long reaction times and with excess of silane. (Table 2, Entries 1 and 2). Switching to microwave heating greatly improved conversion. Under best conditions (Entry 3), approximately one-quarter of the starting material (**3**) was still present after reaction. Moreover, the IR spectrum of the resin recovered from a typical experiment showed an intense signal at 2100 cm^{-1} (Si–H stretching), indicating that the resin still preserved some of its reducing ability. Consequently, in a further attempt to enhance production of **4** a supplementary amount of catalyst **2** (5 mol %) was added to the filtered crude product from Entry 3 and the mixture heated (MW) for another half hour (Entry 4), but to no avail.

Whenever conversion to **4** has reached higher values (Entries 3 and 4), formation of a secondary product (**11**) was apparent from the additional signal observed in the NMR spectrum of the crude reaction mixture. Catalysis by **1** (Entry 5) resulted in lesser production of **4**, while also the secondary product **11** could be evidenced by NMR.

At this point some conclusions became obvious: (i) always approximately one-quarter of the starting material does not react; (ii) catalyst **2** is more active than **1**, in agreement with its stability under the rather harsh conditions (high temperature) employed; (iii) MW-assisted heating leads to better yields than refluxing in dichloromethane; (iv) additional silane has no positive effect.

By virtue of the starting benzyl crotonate (**3**) not being entirely consumed in all experiments with resin-supported silane **8**, a reasonable assumption would be that crotonate **3** partially binds to the resin. To verify this hypothesis, a reaction was carried out (Table 2, Entry 6) using only about one-third (0.75 equiv.) of the usual amount of silane. After 0.5 h, the resin was filtered and an IR spectrum was run, showing an absorption at 1716 cm^{-1} (C=O bond stretching) characteristic for a carboxyl moiety. According to this result, the resin-bound compound was proposed to have the structure **10** indicating the immobilization of the benzyl crotonate (Figure 2). Confirmation came from the further treatment of **10** with Et_3SiH and catalyst **2** that allowed the catalytic cycle to continue, affording fresh product **4** (Table 2, Entry 7; Scheme 4).

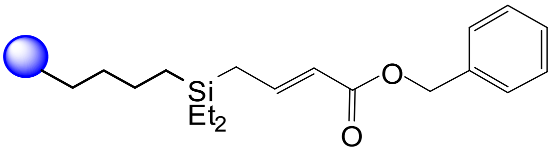


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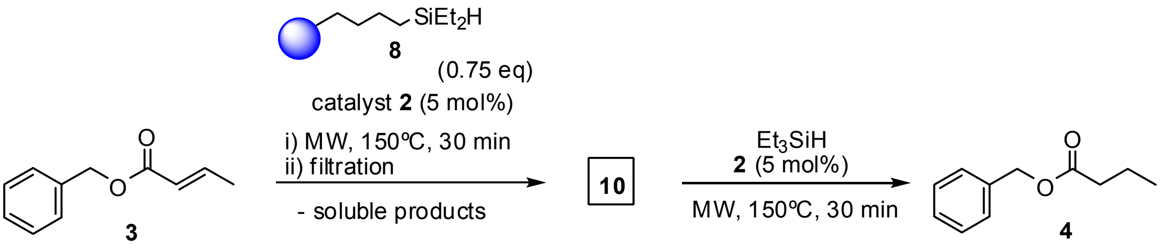
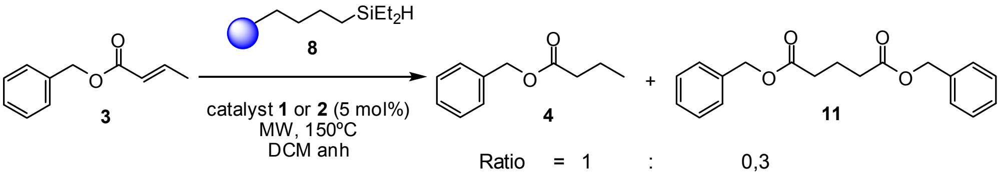
Figure 2. Crotonate **3** bound to the resin (**10**).



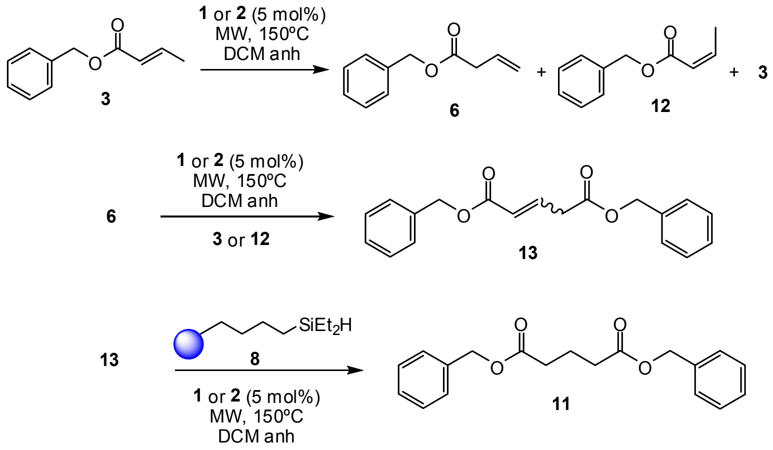
Scheme 4. Generation of the resin-bound crotonate **10** and its further reduction to **4**.

Under the best identified conditions for the “hydrogen-free” reduction of **3** with resin **8** (Table 2, Entries 3 and 5), we found as well a significant amount of a secondary product (**11**), formed along with the desired **4** (molar ration **4**:**11** = 1:0.3) (Scheme 5). Compound **11** was unequivocally deduced by NMR spectroscopy to be 1,5-dibenzyl glutarate.



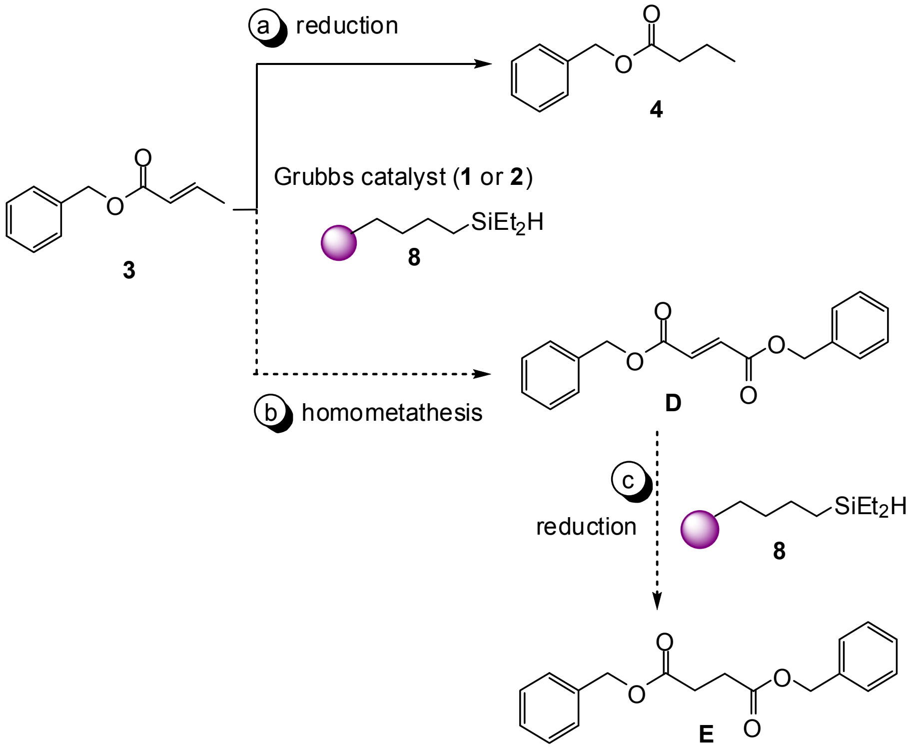
Scheme 5. Reduction of **3** with immobilized silane (resin **8**).

We assume that diester **11** arises by several successive transformations. First, isomerization species, formed in situ from the catalyst, trigger double-bond migration in **3** [23,45,46] to give the terminal olefin **6** and a *trans-cis* isomerization to olefin **12** [23] (Scheme 6). Then, cross-metathesis between olefin **3** (or **12**) and **6**, promoted by the ruthenium alkylidenes originated from **1** or **2**, leads to **13** (*trans* and *cis*). Finally, saturated diester **11** is formed by hydrogenation of **13**, under activation by short-lived Ru-hydride species arising from the catalyst. These species transfer hydrogen atoms from the immobilized silane moieties to the C–C double bond. Formation of **13** was not detected under homogenous phase. This could be attributed to a faster reduction under triethylsilane, as compared with supported silane **8**, and therefore reduction of **3** prevents any further cross-metathesis reaction.



Scheme 6. Cross-metathesis pathway yielding product **11**.

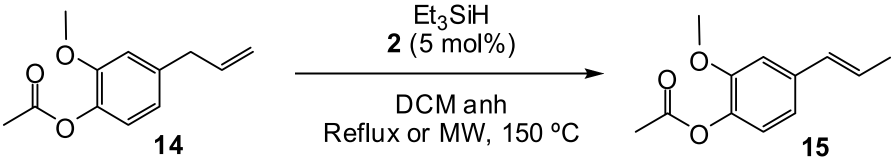
Intriguingly however, homometathesis of **3** (Scheme 7, path b) seems not to intervene, likely because of steric reasons (internal double bond). Indeed, product **E** (that would have been formed through path b and c) has not been detected among the reaction products.



Scheme 7. Hypothetical formation of compound **E** by tandem homometathesis and reduction.

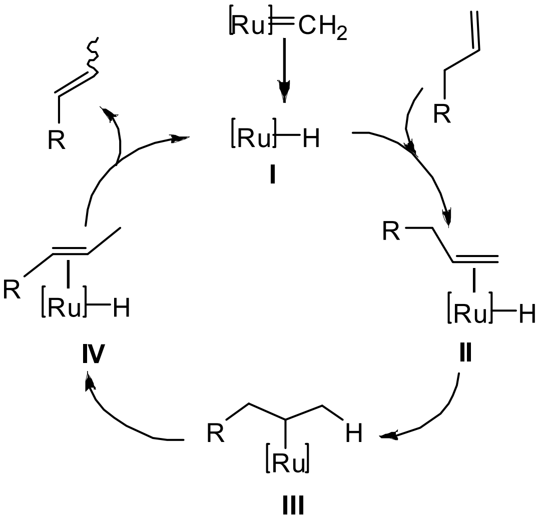
In this intricate catalytic process, the metathesis catalysts (**1** or **2**) generate prevailingly Ru species for isomerization and hydrogenation, leaving, however, some of the initial catalyst to promote cross-metathesis of **3** (or **12**) with **6**. The validity of this interpretation is confirmed by the preponderance of compound **4** among the reaction products.

Inasmuch as olefin **3** has a disubstituted double bond, we next chose, for comparison, the mono-substituted olefin **14** (acetyleugenol) as starting material. Interestingly, on reacting **14** with triethylsilane in solution under the usual conditions, the isomerized compound **15** was obtained as the only product (Scheme 8).



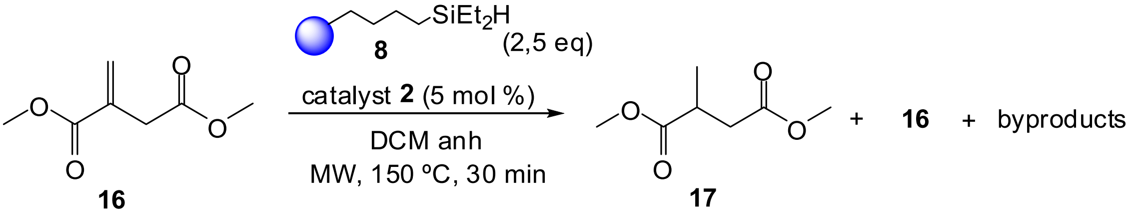
Scheme 8. Isomerization of acetyleugenol (**14**) with Et_3SiH and catalyst **2**.

Anew, this result gives evidence that double-bond migration from the terminal to the internal olefin is taking place [9] (as already seen for isomerization of **3** to **6**). A plausible mechanism for olefin isomerization, as shown in Scheme 9, involves a cyclic pathway, through the intermediacy of species II–IV, similarly to an earlier proposal by Schmidt [4].



Scheme 9. Plausible mechanism for isomerization of terminal olefins to internal olefins (adapted from ref. [4]).

Additional results have been obtained for reduction with resin **8**, of a further substrate, the dimethyl itaconate (**16**) bearing two carbonyl groups and a 1,1-disubstituted olefin (Scheme 10).



Scheme 10. Reduction of dimethyl itaconate (**16**) with immobilized silane (**8**) and catalyst **2**.

After filtering the resin, removing the solvent and drying the product under reduced pressure, we recovered only 27% of the feed (starting materials + catalyst). ^{1}H-NMR analysis of the crude product testified to the presence of the starting **16**, the reduced compound **17**, as well as of several unidentified by-products. IR spectrum of the resin recovered after the reaction revealed an intense bifid absorption at 1718 and 1735 cm^{-1}, corresponding to C=O stretching of the two carbonyls from the dimethyl itaconate. This result supports our assumption that in the catalytic cycle, a C–Si bond (analogous to **10**) is formed between the silane and **16**. Consequently, in case of immobilized silanes, some of the starting material ends up anchored to the solid phase, causing a decrease in the yield.

3. Materials and Methods

3.1. General Considerations

Chemical reagents were purchased from commercial sources and were used without further purification unless noted otherwise. Solvents were analytical grade or were purified by standard procedures prior to use. Resins were purchased from Aldrich. Reactions requiring inert atmosphere were carried out under a high-purity dry nitrogen atmosphere. Solvents from these reactions were transferred with syringe under high-purity dry nitrogen pressure. Reagents were transferred in that way or with Gilson micro-pipettes of 100–1000 μL or 20–200 μL.

3.2. Instrumental and Physical Data

^{1}H-NMR spectra were recorded in a Bruker Avance spectrometer (Bruker Analytik GmbH, Karlsruhe, Germany) at 300 MHz, in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. ^{13}C-NMR spectra were recorded on the same apparatus at 75 MHz with $CDCl_3$ as solvent and reference (76.9 ppm). Chemical shifts (δ) are reported in ppm upfield from TMS and coupling constants (*J*) are expressed in Hertz.

In the preparation of the samples for ^{13}C gel-phase NMR, 50–80 mg of resin is placed in a standard NMR tube and 0.5 mL of $CDCl_3$ is slowly added in order to obtain a gel, which is homogenized by sonication. Spectra were run according to the literature [47].

Mass spectra were recorded on a Shimadzu QP2010 Plus apparatus (Shimadzu Corporation, Kyoto, Japan) at an ionization voltage of 70 eV equipped with a SPBTM-1 capillary column (internal diameter 0.25 mm, length 30 m). High-resolution mass spectra were obtained with a Bruker MicroTOF-Q II instrument (Bruker Daltonics, Billerica, MA, USA). Detection of the ions was performed in electrospray ionization, positive ion mode.

Solid-phase reactions were carried out in polypropylene cartridges equipped with a frit (Supelco, Bellefonte, PA, USA), unless reflux or microwave conditions were required, in that case standard glassware was used. All solid-phase reaction mixtures were stirred at the slowest rate.

The microwave-assisted chemical transformations were performed using a CEM Discover LabMate reactor (CEM Corporation, Matthews, NC, USA), using the standard heating program in which the operator chooses the final temperature and the equipment automatically adjusts the delivered power in order to maintain the final temperature constant.

Infrared spectra were recorded on a Shimadzu FT-IR spectrometer model 8101 (Shimadzu Corporation, Kyoto, Japan). The resin samples were measured as dispersions in KBr discs, made by compression of a mixture finely powdered in an agate mortar, the approximate composition being 3 mg of sample in 100 mg of KBr.

3.3. Synthetic Procedures

3.3.1. Synthesis of 4-(Diethylsilylbutyl) Polystyrene Resin (**8**)

Merrifield resin (3.8 mmol/g, 1.9 mmol, 0.5 g) was swelled under gentle stirring in anhydrous toluene (20 mL). Allylmagnesium chloride (2M in tetrahydrofuran [THF], commercial solution) was added (2.6 equiv, 4.92 mmol, 2.5 mL). The mixture was stirred at 60 °C for 12 h. After filtration, the resin was washed with THF, 20 mL of a THF/HCl 1N solution (3/1) were added, and the mixture was stirred for 12 h at 45 °C. After filtration, the resin was sequentially washed with THF (3 × 10 mL), MeOH (3 × 10 mL), CH_2Cl_2 (3 × 10 mL) and finally dried under high vacuum. The resin was analyzed by IR and ^{13}C gel-phase NMR in order to confirm formation of the intermediate compound and then the second stage of synthesis was carried out: A solution of Wilkinson catalyst [$RhCl(PPh_3)_3$] (0.4 mol %, 8×10^{-3} mmol, 8 mg) in 20 mL of anhydrous toluene was added to the resin and the mixture was stirred for several minutes. The mixture was then treated with excess of Et_2SiH_2 (2 equiv., 4 mmol, 0.5 mL) and left to stir for 2 h at r.t. After that, the resin was filtered and washed with toluene (4 × 15 mL), THF (4 × 15 mL), DCM (4 × 15 mL) and finally dried under high vacuum. IR spectroscopy and ^{13}C gel-phase NMR were performed to corroborate if the expected resin **8** was obtained [44].

3.3.2. General Procedure for Olefin Reduction in the Presence of Grubbs Catalysts and Triethylsilane

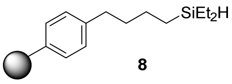
The corresponding olefin and Et_3SiH were added to a microwave tube equipped with stirrer and purged for a few minutes with N_2. Then, 3 mL of anhydrous DCM and 5 mol % of the Grubbs catalyst were added. The tube was capped and the reaction mixture was subjected to microwave heating at 150 °C (maximum power = 120 W) for the corresponding time in each case. After heating, the reaction crude was concentrated and dried under high vacuum.

3.3.3. General Procedure for Olefin Reduction in the Presence of Grubbs Catalysts and Resin-Immobilized Silane (8)

The corresponding olefin and the 4-(diethylsilylbutyl) polystyrene resin (**8**) were added to a microwave tube with stirrer and purged for a few minutes with N_2. Then, 3 mL of anhydrous DCM and 5 mol % of the Grubbs catalyst were added. The tube was capped and the reaction mixture was heated at 150 °C (maximum power = 120 W). After the time set for each case, the reaction crude was filtered through a sintered glass filter and the liquid was collected in a round-bottom flask, concentrated and then dried under high vacuum.

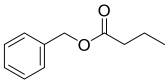
In the case of the reaction with dimethyl itaconate (**16**), the ^{1}H-NMR spectrum of the reaction crude was analyzed and compared to the starting material spectrum. It was verified that product **17** was obtained since the characteristic signal at 0.97 ppm of the three protons of methyl group was evidenced. Nevertheless, the reaction resulted in the formation of many by-products and there was still some starting material **16** in the crude.

3.4. Analytical Data



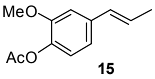
8

4-(Diethylsilylbutyl) polystyrene resin (**8**). IR (KBr) ν_{max} (cm^{-1}) 3024; 2916; 2848; 1637; 1600; 1560; 1490; 1448; 906; 756; 592. ^{13}C gel-phase NMR ($CDCl_3$, 75 MHz): δ = 145.6, 138.6, 128.2, 125.9, 115.0, 46.4, 44.2, 40. 7, 35.9, 53.3.



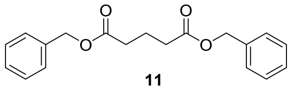
4

Benzyl butyrate (**4**). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.35 (m, 5H), 5.12 (s, 2H), 2.34 (t, *J* = 7.4 Hz, 2H), 1.87 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 173.5, 136.2, 128.5, 128.2, 128.1, 128.1, 66.0, 36.21, 18.5, 13.7. GC-MS (EI, 70 eV): *m*/*z* (%) = 178 [M$^+$] (15), 160 (1), 108 (94), 91 (100), 71 (35), 65 (26).



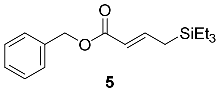
15

Acetyl isoeugenol (**15**). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 6.93 (m, 5H), 6.37 (d, *J*=15.7 Hz, 1H), 6.20 (m, 1H), 3.83 (s, 3H), 2.30 (s, 3H), 1.88 (d, *J* = 6.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 169.2, 151.0, 138.6, 137.1, 130.5, 126.1, 122.7, 118.4, 109.6, 55.8, 20.7, 18.4.



11

1,5-Dibenzyl glutarate (**11**). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.34 (m, 10H), 5.11 (s, 4H), 2.43 (t, *J* = 7.4 Hz, 4H), 1.99 (q, *J* = 7.4 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 172.7, 135.9, 128.6, 128.3, 128.2, 66.2, 33.3, 20.1.



5

Benzyl (4-triethylsilyl)-*trans*-crotonate (**5**). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.35 (m, 5H), 7.12 (dt, *J* = 15.3 Hz, *J* = 8.9 Hz, 1H), 5.73 (d, *J* = 15.4 Hz, 1H), 5.16 (s, 2H), 1.77 (d, *J* = 8.9 Hz, 2H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.57 (q, *J* = 7.9 Hz, 6H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 166.7, 149.2, 136.4, 128.2, 128.1, 128.0, 118.4, 65.7, 19.8, 3.2, 1.0. HRMS (ESI) *m*/*z* 313.15794 [$(M + Na)^+$; calcd. for $C_{17}H_{26}NaO_2Si$: 313.15943].

4. Conclusions

In summary, this work focuses on the complex competition between metathesis and non-metathesis processes, here applied to both solution and solid-phase silane reagents. The reactions occur between different olefin substrates and silanes, in presence of the Grubbs or Hoveyda–Grubbs ruthenium catalysts **1** or **2**. Catalysis of non-metathetic transformations (isomerization, "hydrogen-free" reduction, silylation) is being ascribed to clear-cut ruthenium species arising from promoters **1** and **2**, under the experimental conditions. These transient catalytic species differ from the Ru-alkylidenes responsible for metathesis. Reaction pathways accounting for these simultaneous processes have been evidenced. An important finding of this research unveils the concurrent binding of the olefin to the silylated resin, bringing about an adverse effect on the overall yield of the reactions with a solid-phase silane reagent. Follow-up investigations on tandem metathetic/non-metathetic reactions of olefins, comparatively run in solution and solid-phase with ruthenium catalysts, are currently in progress.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/7/4/111/s1, Figure S1: ^{1}H NMR of a mixture of compounds **4** and **5** in $CDCl_3$, Figure S2: ^{13}C NMR of a mixture of compounds **4** and **5** in $CDCl_3$, Figure S3: HH-COSY NMR of a mixture of compounds **4** and **5** in $CDCl_3$, Figure S4: HSQC NMR of a mixture of compounds **4** and **5** in $CDCl_3$, Figure S5: HMBC NMR of a mixture of compounds **4** and **5** in $CDCl_3$, Figure S6: TOCSY NMR of a mixture of compounds **4** and **5** in $CDCl_3$, the experiment was carried out irradiating H-5 of compound **5**, Figure S7: TOCSY NMR of a mixture of compounds **4** and **5** in $CDCl_3$, the experiment was carried out irradiating H-4 of compound **5**, Figure S8: Experimental HRMS of compound **5**, Figure S9: Simulated HRMS of compound **5**, Figure S10: ^{1}H NMR of compound **6** in $CDCl_3$, Figure S11: ^{13}C NMR of compound **6** in $CDCl_3$, Figure S12: HSQC NMR of compound **6** in $CDCl_3$, Figure S13: ^{13}C gel phase NMR of resin **8** in $CDCl_3$, Figure S14: IR of resin **8** in KBr pellet, Figure S15: ^{1}H NMR of compound **11** in $CDCl_3$, Figure S16: ^{13}C NMR of compound **11** in $CDCl_3$, Figure S17: HSQC NMR of compound **11** in $CDCl_3$.

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