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Formation of allylsilanes from $Cl_2[P(C_6H_{11})_3]_2Ru{=}C(R)H$ and vinylsilanes—β-SiR'_3 elimination from ruthenacyclobutanes as a terminating step in olefin cross-metathesis

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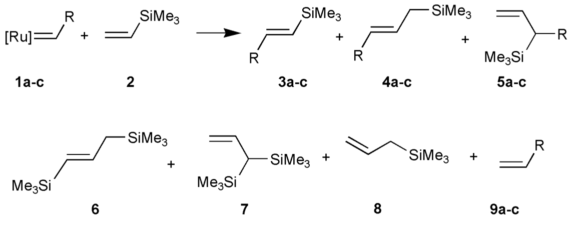
Stoichiometric reactions of the Grubbs carbene complex $[Cl_2\{P(C_6H_{11})_3\}_2Ru{=}C(Ph)H]$ with vinylsilanes, $H_2C{=}C(SiMe_nR_{3-n})H$ (R = Ph, OEt; n = 1, 2, 3), afford metathesis products and allylsilanes formed by β-SiR_3 elimination followed by reductive elimination; the formation of allylsilanes constitutes a terminating step in the Ru-catalysed cross-metathesis of olefins with methylsubstituted vinylsilanes.

Metallacyclobutanes[1] play an important role in a number of stoichiometric and catalytic transformations. Two of the catalytically most important reaction modes of metallacyclobutanes are (a) reductive elimination to give cyclopropanes and a metal–ligand fragment[2] and (b) reductive decoupling to form an olefin–carbene complex (olefin metathesis).[3] In these reactions the metallacyclobutanes are formed as intermediates by addition of the C=C bond of an olefin to the M=C bond of an $L_nM{=}C(R)R'$ complex. Several types of olefin metathesis are known, such as ring-opening metathesis polymerisation, self- and cross-metathesis of linear olefins, acyclic diene metathesis (ADMET), and ring-closing metathesis (RCM).[3]

We recently reported[4] on the highly selective cross metathesis of styrene $H_2C{=}C(Ph)H$, with several vinylsilanes $H_2C{=}C(SiR_3)H$, to give (E)-$H(Ph)C{=}C(SiR_3)H$ and ethylene catalysed by the Grubbs catalyst $[Cl_2\{P(C_6H_{11})_3\}_2Ru{=}C(Ph)H]$ (**1a**).[5] Very high conversions even at rt were observed when R = OR′ (R′ = Et, $SiMe_3$); however, the conversion significantly decreased with increasing substitution of Me for OR′.[4] To determine the reason for the decreasing selectivity we studied the stoichiometric reaction of **1a** with various vinylsilanes and now report on (a) the first evidence for β-silyl migration in metallacyclobutanes, (b) the very high selectivity of β-SiR_3 *versus* β-H migration and (c) hints for β-migration as the terminating step thus limiting the efficiency of the catalyst.

When an equivalent of trimethylvinylsilane (**2**) was added to a solution of **1a** in C_6D_6 a smooth reaction was observed.† After 6 h at rt 98% of **2** and 99% of **1a** had been consumed. A detailed analysis of the organic reaction products revealed the formation of 15% of **3a**, 57% of **4a**, 6% of **5a**, in addition to small amounts of **6** (5%), **7** (2%), **8** (5%), **9a** (2–5%) (Scheme 1) and unidentified Ru complexes. Cyclopropanes were not detected.



R = Ph (**a**), H (**b**), Me (**c**); [Ru] = $Cl_2[P(C_6H_{11})_3]_2Ru$

Scheme 1

Only compounds **3a** and **9a** are those expected from olefin metathesis. All other products (**4a–8**) are allyl derivatives containing the C_3 fragment of the metallacycle. Obviously, the metallacycle formed by addition of **2** to the Ru=C bond of **1a** breaks down by two different pathways: (a) reductive decoupling to give the metathesis products **3a**, **9a** and a [Ru]=C(R)H species and (b) elimination of an allylsilane derivative and formation of a [Ru] fragment.

Pathway (b) causes a decrease of the catalytically active [Ru]=C(R)H species and presumably is the most important factor in reducing the efficiency of the catalytic system. The conclusion is supported by the following observation: When Me in **2** is replaced stepwise by OEt, both the ratio of the metathesis product (type **3**) to the allyl derivative (type **4**) in the stoichiometric reaction [0.26 ($SiMe_3$), 0.68 ($Si(OEt)Me_2$), 13 ($Si(OEt)_2Me$)] and the cross-metathetical conversion of styrene to vinylsilane mixtures catalysed by **1** drastically increase. Analogously, a strong shift toward the metathesis product is observed when Me is stepwise displaced by Ph.

The reactions of **2** with the methylidene complex **1b** and the ethylidene complex **1c** instead of **1a** proceeded similarly, albeit more slowly. The reaction rate decreased in the series **1a** > **1b** > **1c**. Again mixtures of metathesis products and allyl derivatives were obtained. The reactions of **2** with **1b** and **1c** were accompanied by a substrate-independent decomposition of the Ru complexes[6] which gave rise to a reduction in the conversion of **2** (41% for **1b** and 35% for **1c**, each after 6 h). Within error limits, the product distribution after 6 h was the same as that after 18 h.

The formation of the major allyl derivative (**4a**) in the reaction of **1a** with trimethylvinylsilane (**2**) can be explained in two different ways: (i) by β-$SiMe_3$ elimination to give an allyl(silyl) complex (see Scheme 2: **C**/**D**) followed by reductive elimination or (ii) by β-H elimination to give a hydrido(α-silylallyl) complex (Scheme 2: **E**/**F**) again followed by reductive elimination. The labeling experiment (Scheme 2) allows exclusion of pathway (ii). The ^{2}H-NMR spectrum of the products obtained from the reaction of **1a** with $H_2C{=}C(D)SiMe_3$ (**2**-d_1) exhibited only signals in the *olefinic* region. From the absence of signals in the *aliphatic* region it follows that **4a′**-d_1 has not been produced. The formation of more than 1% of **4a′**-d_1 (with respect to **4a′**-d_1) would have been detected. Another product of pathway (ii), compound **10**, has not been identified among the reaction products in earlier experiments (see Scheme 1). These results indicate that there is a strong preference for β-SiR_3 elimination over β-H elimination. In fact, products derived from β-H elimination have not been detected in the stoichiometric experiments. Thus the ratio **4a**/**5a** = 57 : 6 presumably reflects the relative stabilities of different allyl(silyl) complex intermediates **C** and **D**.

The bis(silyl)allyl derivatives **6** and **7** are secondary products derived from the reaction of [Ru]=C($SiMe_3$)H with **2**. Their formation establishes that [Ru]=C($SiMe_3$)H species are also formed in the reaction of **1** with **2** as we proposed earlier.[4] Until

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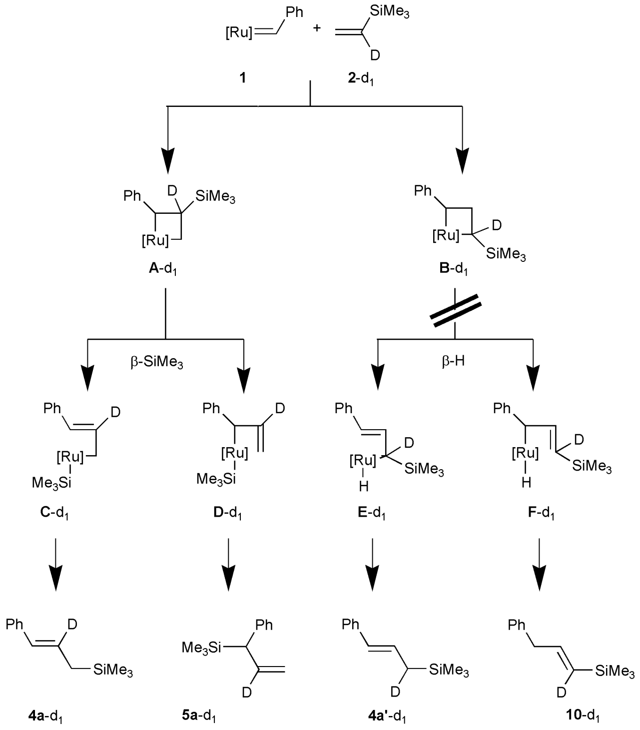

Scheme 2

now, all our attempts to synthesise $[Cl_2\{P(C_6H_{11})_3\}_2Ru{=}C(SiMe_3)H]$ or to spectroscopically detect $Ru{=}C(SiMe_3)H$ species in the cross-metathesis of vinylsilanes with styrene catalysed by **1** have failed.[4]

Our results demonstrate that β-SiR_3 elimination in β-SiR_3-substituted ruthenacyclobutanes followed by reductive elimination strongly competes with olefin metathesis and thus presumably is the most important factor limiting the catalytic efficiency of the system. The migratory aptitude considerably decreases in the series $SiMe_3 > Si(OEt)Me_2 > Si(OEt)_2Me$ and $SiMe_3 > Si(Ph)Me_2 > Si(Ph)_2Me$. Although there is a strong preference for SiR_3 migration compared to H migration it seems likely that β-H elimination and subsequent reductive elimination in systems without a SiR_3 substituent could also drain the active species from the catalytic cycle and thus limit the turnover number in cross-metathesis.

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Notes and references

† Typically, in an NMR tube 1.21×10^{-5} mol of vinylsilane was added by syringe to a solution of $[Cl_2\{P(C_6H_{11})_3\}_2Ru{=}C(Ph)H]$ (0.01 g, 1.21×10^{-5} mol) and anthracene (internal standard) dissolved in 0.65 ml of C_6D_6. The reactions were followed by ^{1}H-NMR spectroscopy for 6 h. Conversions and selectivities were calculated using the internal standard method.[7] Products were identified by GC-MS spectra and by a comparison of their ^{1}H NMR spectra and their retention times (GC) with those of authentic samples.

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