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Regio- and stereoselective hydrosilylation of terminal alkynes using Grubbs' first-generation olefin-metathesis catalyst†

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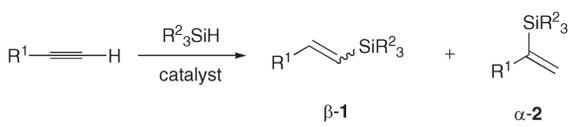
Grubbs' first-generation, Ru metathesis complex 3 catalyses the hydrosilylation of terminal alkynes. The reaction exhibits an interesting selectivity profile that is dependent on the reaction concentration and more importantly on the silane employed.

Introduction

Vinylsilanes have emerged as powerful intermediates in organic synthesis, and further advances continue to enhance their synthetic utility.[1] Most notably, they now make viable substitutes for highly toxic vinylstannanes in Pd-catalysed cross-coupling reactions.[2] They have also been successfully employed in ring-closing-metathesis[3] and cross-metathesis[4] reactions. However, the synthetic utility of this functionality remains dependent on being able to prepare the starting vinylsilane with high levels of regio- and stereocontrol.

Although vinylsilanes can be prepared in a number of ways,[5] the transition-metal-catalysed hydrosilylation of alkynes has proven to be the most powerful.[6] Hydrosilylation of a terminal alkyne using a silane, R_3SiH, in the presence of a transition-metal catalyst can provide up to three, isomeric vinylsilane products, β-(*E*)-**1**, β-(*Z*)-**1**, and α-**2** (Scheme 1).

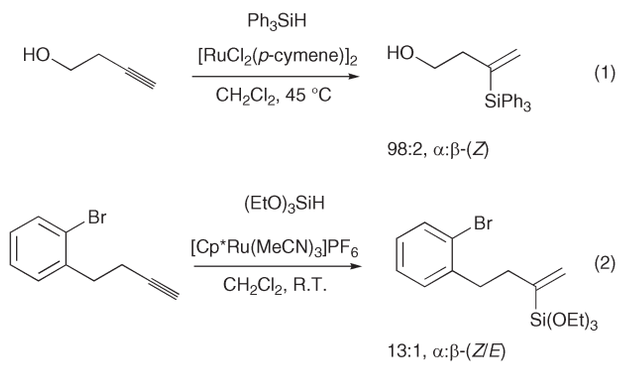


Scheme 1 Hydrosilylation of terminal alkynes provides three isomeric vinylsilane products.

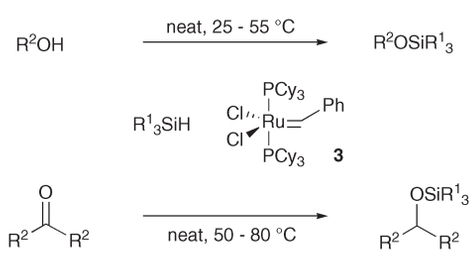
The regio- and stereochemical outcome of this reaction depends on several factors including the choice of catalyst (the metal and ligands), the substituents on both reacting partners, and to a lesser extent, on the reaction conditions employed (reaction temperature, solvent and catalyst loading). The β-(*E*)-stereoisomer, β-(*E*)-**1**, is best obtained using Pt-based complexes,[7] whilst the selective formation of the stereoisomeric β-(*Z*)-vinylsilane, β-(*Z*)-**1**, is generally achieved using Rh- and Ru-based catalysts.[8,9] The formation of the third regioisomer, α-**2**, is best accomplished by incorporating a functionality in the substrate, which can coordinate to the metal complex and deliver the silicon and hydrogen substituents to the alkyne in an intramolecular fashion [Scheme 2, eqn. (1)].[9c] In the absence of such a directing group, the selective formation of vinylsilane α-**2** has proven to be much more difficult; indeed Trost and Ball only recently reported the first example of a non-directed alkyne hydrosilylation route to this regioisomer using a cationic Ru complex, $[Cp^*Ru(MeCN)_3]PF_6$ [Scheme 2, eqn. (2)].[9b] Efficient catalysts that effect the selective formation of vinylsilane, α-**2** (as well as the two other stereoisomers, β-(*E*)-**1** and β-(*Z*)-**1**) therefore remain highly desirable.[9a,b]

Results and discussion

Over the last decade, the metathetic behaviour of Grubbs' so-called 'first-generation' Ru-catalyst **3** (Scheme 3) has been exploited in numerous synthetic applications.[10] Whilst metathesis remains the most important application for this class of Ru alkylidene complex, a growing number of other processes are also mediated by Grubbs' catalyst.[11] For example, Lee and co-workers recently reported that **3** displays excellent catalytic activity in the hydrosilylation of carbonyl compounds and dehydrogenative condensation of alcohols and silanes (Scheme 3).[12]



Scheme 2 Selective hydrosilylation for the α-**2** regioisomer is possible in some cases.



Scheme 3 Application of Grubbs' catalyst **3** in hydrosilylation of ketones and silylation of alcohols.

Prompted by these results we postulated that Grubbs' catalyst **3** might also catalyse an alkyne hydrosilylation. We were therefore delighted to observe that heating equimolar quantities of Et_3SiH and 1-hexyne at 60 °C, in the presence of 2.5 mol% **3** and absence of solvent, resulted in the rapid consumption (<30 min) of both starting materials (as judged by ^{1}H-NMR) and the formation of a 11 : 64 : 25 mixture of all three isomeric vinylsilane products, β-(*E*)-**1**, β-(*Z*)-**1** and α-**2** (entry 1, Table 1). Reducing the reaction temperature to 22 °C (RT) led to an increased reaction time and decrease in selectivity for the β-(*Z*)-stereoisomer (entry 2, Table 1). Since we observed a further reduction on continued stirring (*c.f.* entries 2 and 3, Table 1), we propose that this erosion in selectivity is most likely a result of product-scrambling on prolonged exposure to the Ru catalyst.[13]

In an attempt to improve the selectivity, we carried out the reaction in a range of solvents at 40 °C and RT. The results of this preliminary solvent screen are summarised in Table 1. With the exception of MeCN, which generated a range of undetermined products, all the solvents tested proved suitable for allowing hydrosilylation, providing in all cases the β-(*Z*) stereoisomer as the major product. The fact that we could use acetone as a solvent shows that hydrosilylation of the alkyne is much more rapid than the

† Electronic supplementary information (ESI) available: characterisation data and NMR spectra for novel vinylsilanes. See http://www.rsc.org/suppdata/ob/b4/b409832c/

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Table 1 Investigating the effect of solvent, reaction concentration and temperature on the hydrosilylation of 1-hexyne with Et_3SiH

Entry	Solvent	Reaction temperature/°C	Reaction concentration/M	Time[a]/h	% Conversion[b]	Ratio[c] β-(*Z*) : α : β-(*E*)
1	no solvent	60	—	0.5	100	64 : 25 : 11
2	no solvent	RT	—	12[d]	100	53 : 12 : 35
3	no solvent	RT	—	48[d]	100	37 : 33 : 30
4	THF	40	1	2	100	84 : 16 : trace
5	THF	RT	1	12	100	88 : 12 : trace
6	CH_2Cl_2	40	1	2	100	67 : 33 : trace
7	CH_2Cl_2	RT	1	12	100	68 : 18 : 14
8	MeCN	40	1	2	100	[e]
9	hexane	RT	1	12	100	56 : 11 : 33
10	acetone	40	1	2	99	89 : 10 : 1
11	acetone	40	0.1	4	100	93 : 6.5 : 0.5
12	acetone	40	0.01	8	23	100 : trace : trace
13	acetone	RT	10	1	100	80 : 11 : 9
14	acetone	RT	1	4	95	89 : 9 : 2
15	acetone	RT	0.1	33	78	95 : 4.5 : 0.5
16	PhMe	40	1	1	100	83 : 15 : 2
17	**PhMe**	**40**	**0.1**	**2**	**100**	**96 : 4 : trace**
18	PhMe	40	0.01	8	49	93 : 7 : trace
19	PhMe	RT	10	1	100	74 : 22 : 4
20	PhMe	RT	1	2	100	78 : 20 : 2
21	PhMe	RT	0.1	8	92	90 : 10 : trace

[a] In some instances the reaction was probably complete well before this time. [b] Based on complete consumption of 1-hexyne. [c] Ratio calculated by analysis of the crude reaction mixture by ^{1}H-NMR and/or by GC after the time stated in the Table. [d] Both starting materials were still present after 2 h but had been completely consumed after 12 h. [e] Range of undetermined products in addition to the β-(*Z*)-stereoisomer.

potentially competing reaction with the ketone functionality present in the solvent (Scheme 3). Carrying out the reaction at elevated temperature, instead of at RT, once again led to an increase in the reaction rate although had relatively little effect on the selectivity.

We next focused on two rather different solvents, namely toluene and acetone, that had performed well in our initial solvent screen, and investigated the hydrosilylation of 1-hexyne with Et_3SiH at different concentrations and reaction temperatures. The results are summarised in Table 1. Using both solvents, we were pleased to observe a significant improvement in both the regio- and stereoselectivity of the reaction, in favour of the β-(*Z*)-product, on decreasing the reaction concentration. Reactions performed in toluene were more rapid than those carried out in acetone, although our best selectivities were obtained using acetone and a 0.01 M reaction concentration (entry 12, Table 1). However in this case, the rate of reaction proved to be unacceptably low. When we performed the same investigation with phenylacetylene, the reaction was already highly selective for the β-(*Z*)-product at 1 M in both acetone and toluene; reducing the reaction concentration further simply decreased the rate of hydrosilylation. Although we had previously observed scrambling of the product stereochemistry when the reaction had been performed in the absence of solvent (entries 1–3, Table 1), this proved not to be a problem when the reaction was carried under these more dilute conditions: for example, no change in the ratio of products obtained from the reaction between 1-decyne and $PhMe_2SiH$ (entry 10, Table 2) was observed when the reaction mixture was stirred for a further 18 h after complete consumption of starting materials. Whilst carrying out this study we also observed the formation of Et_3SiOH as a by-product especially when acetone was used as solvent. However, the use of 1.1 equivalents of the silane was sufficient to ensure complete consumption of the alkyne starting material.

We next investigated a range of alkynes and silanes using our optimised reaction conditions of toluene as solvent, a reaction temperature of 40 °C and concentration of 0.1 M. The results are summarised in Table 2. Under these conditions and with 2.5 mol% catalyst loading, 1-decyne and phenylacetylene both reacted smoothly with Et_3SiH to provide the β-(*Z*)-stereoisomer as the major product (entries 1 & 2, Table 2). Reaction with 3,3-dimethylbut-1-yne showed that bulkier alkyne substituents are also tolerated (entry 3, Table 2), although in this case the major stereoisomer was the β-(*E*)-product. This presumably reflects the high energy of the TS leading to the β-(*Z*)-stereoisomer arising from the increased steric hindrance provided by the bulky ^{t}Bu substituent (although see mechanistic discussion below for an alternative interpretation). This change in selectivity from the (*Z*)- to (*E*)-stereoisomer in the case of 3,3-dimethylbut-1-yne has been observed previously.[9a] Mindful of the increased length of a C–Si bond relative to a C–C bond,[14] we hoped that silyl acetylenes might also undergo hydrosilylation;

Table 2 Hydrosilylation of terminal alkynes using a range of silanes[a]

Entry	R^1	Silane	Ratio[b]	Yield[c] (%)
1	C_8H_{17}	Et_3SiH	91 : 9 : tr	86
2[d]	Ph	Et_3SiH	95 : 5 : tr	74
3	^{t}Bu	Et_3SiH	tr : tr : 100	70[e]
4	TIPS	Et_3SiH	[f]	[f]
5	CO_2Me	Et_3SiH	[f]	[f]
6[g]	CH_2OBz	Et_3SiH	1 : 97 : 2[h]	46
7[d]	$CH_2OTBDMS$	Et_3SiH	16 : 63 : 21	51
8[i]	CH_2CH_2OBz	Et_3SiH	86 : 14 : tr	66
9	$CH_2CH_2OTBDMS$	Et_3SiH	94 : 6 : tr	90
10	C_8H_{17}	$PhMe_2SiH$	69 : 24 : 7	87
11	Ph	$PhMe_2SiH$	95 : tr : 5	81
12[g]	CH_2OBz	$PhMe_2SiH$	tr : 93 : 7	62
13[d]	$CH_2OTBDMS$	$PhMe_2SiH$	6 : 71 : 23	73
14	CH_2CH_2OBz	$PhMe_2SiH$	53 : 28 : 19	78
15	$CH_2CH_2OTBDMS$	$PhMe_2SiH$	66 : 17 : 17	79
16	CH_2OH	$PhMe_2SiH$	tr : 100 : tr	59[j]
17	C_8H_{17}	$(EtO)_3SiH$	17 : 73 : 10	>90[k]
18	Ph	$(EtO)_3SiH$	[f]	[f]
19[g]	CH_2OBz	$(EtO)_3SiH$	tr : 97 : 3	>90[k]
20[g]	$CH_2OTBDMS$	$(EtO)_3SiH$	10 : 80 : 10	>90[k]
21[i]	CH_2CH_2OBz	$(EtO)_3SiH$	5 : 92 : 3	>90[k]
22	$CH_2CH_2OTBDMS$	$(EtO)_3SiH$	5 : 92 : 3[l]	>85[k]

[a] Reaction concentration at 0.1 M and 2.5 mol% **3** unless stated otherwise. All reactions were generally complete within 10 h. [b] Ratio: β-(*Z*) : α : β-(*E*) determined on the crude reaction mixture by ^{1}H-NMR (tr = trace quantities only). [c] Isolated yield of the vinylsilane mixture after column chromatography. [d] Reaction performed with 2.5 mol% catalyst and 1 M reaction concentration. [e] The low yield can be attributed to loss of the volatile alkyne starting material. [f] Reaction afforded a range of undetermined products in addition to small amounts of the desired vinylsilanes. [g] Reaction performed with 5 mol% catalyst at 1 M reaction concentration. [h] Ratio determined on reaction mixture after passing through a silica plug. [i] Reaction performed with 5 mol% catalyst at 0.1 M reaction concentration. [j] 11% of the silyl ether vinylsilane product was also isolated. [k] Crude reaction yield (see Supplementary Information for crude NMR spectra). [l] Partially overlapping vinylic hydrogen resonances in the crude ^{1}H-NMR for β-(*Z*) and β-(*E*) rendered calculation of the relative ratio of these two isomers difficult; however the α : β ratio for this entry is accurately 92 : 8.

however, in contrast to 3,3-dimethylbut-1-yne, TIPS-acetylene proved to be a far poorer substrate, reacting very slowly, even in the presence of 10 mol% catalyst and at 10 M reaction concentration, to provide a range of undetermined products along with recovered starting material. This suggests that electronic factors are also important in governing the reaction efficiency. This was further confirmed when running the alkyne into conjugation with an electron-withdrawing ester substituent also failed to provide the desired hydrosilylation products (entry 5, Table 2). A weaker electron-withdrawing hydroxymethyl substituent, however, was tolerated: the TBDMS ether of propargyl alcohol reacted well under our standard conditions (entry 7, Table 2); the more electron-withdrawing benzoate derivative required an increase in catalyst loading (5 mol%) to ensure complete conversion of starting material in a reasonable time (entry 6, Table 2). Significantly, we observed a reversal in the regioselectivity in these two cases, with the α-stereoisomer now predominating. By inserting an additional methylene group between the electron-withdrawing oxygen functionality and reacting alkyne, we were able to restore reactivity and also selectivity for the β-(*Z*)-stereoisomer (entries 8 & 9, Table 2). In the case of propargyl benzoate, we propose that the proximal carbonyl functionality acts as a directing group in the hydrosilylation reaction.[15] However, since bulky silyl protecting groups are widely used to suppress the Lewis basicity of alcohols, the fact that the TBDMS ether of propargyl alcohol also provides the α-stereoisomer as the major product, whereas the TBDMS ether of homopropargylic alcohol provides the β-(*Z*)-stereoisomer, suggests that an electronic polarisation of the alkyne might also be capable of governing the regioselectivity of our reaction.

Changing the silane from Et_3SiH to $PhMe_2SiH$ provided similar results although in general with reduced levels of selectivity (entries 10–15, Table 2). Interestingly, reaction of propargyl alcohol with $PhMe_2SiH$ provided the α-stereoisomer as the major product in 59% yield [*c.f.* eqn. (1), Scheme 2] along with 11% of the same vinylsilane regioisomer in which the alcohol had also been silylated (entry 16, Table 2).

Reaction with $(EtO)_3SiH$ would provide a synthetically very useful vinylsilane product that can be used in Pd-catalysed cross-coupling reactions.[2] We were therefore pleased to see that this silane reacted similarly well, although in this case, we observed a dramatic reversal in the regioselectivity of the reaction; in *all* cases the α-regioisomer was obtained as the major product with good to excellent levels of selectivity. These results therefore provide a rare example of a hydrosilylation reaction that is regioselective for the α-stereoisomer, irrespective of whether a directing group is present or not.

It is interesting to speculate on the nature of the active catalyst in our hydrosilylation reaction and a mechanism of reaction that rationalises the observed selectivity differences involving various substrates and silanes. Asking whether or not a ruthenium alkylidene complex is the active catalyst is a useful place to open the discussion. When we used ^{31}P-NMR spectroscopy to monitor the hydrosilylation reaction between 1-hexyne and Et_3SiH in the presence of 5 mol% Grubbs' catalyst **3**, the only major resonance observed throughout the experiment, was that for the PCy_3 ligands in the ruthenium alkylidene complex. This might suggest that **3** provides the resting state in the catalytic cycle and a coordinatively unsaturated ruthenium alkylidene complex **4**, generated by loss of a phosphine ligand, for example, is the active catalyst. If this is the case, reaction might therefore commence with the formation of the ruthenium silyl intermediate **5** through σ-metathesis between the silane and the ruthenium alkylidene **4**, in analogy with the classical Chauvin mechanism involving olefins (Fig. 1).[16] Subsequent insertion of the alkyne into the Ru–Si bond would be expected to proceed in a *syn* fashion to provide a vinyl ruthenium complex **6**.[8c,17] In the case of terminal alkynes containing small R groups—and in analogy to related systems—this intermediate would be expected to isomerise rapidly to the net *trans* metallametalation product **7** to relieve steric interactions between the silyl group and ruthenium complex.[8c,17b,c,e] β-Hydride elimination would then provide the β-(*Z*)-stereoisomer vinylsilane product and regenerate the ruthenium alkylidene complex **4** thereby completing the catalytic cycle. If the rate of isomerisation of **6** to **7** is low, as would be expected for alkynes containing sterically demanding substituents such as 3,3-dimethyl-but-1-yne, then direct β-hydride elimination from the *syn* metallametalation intermediate **6** would nicely account for the formation of the β-(*E*) stereoisomer for this class of alkyne substrates. Further evidence for the formation of a vinyl ruthenium intermediate such as **7** comes from our identification of a silylacetylene by-product **8**, which we observed in trace amounts (<1%) by GC-MS analysis of the products derived from the reaction between Et_3SiH and 1-decyne. The formation of this by-product can be rationalised by invoking a competing β-hydride elimination on the vinyl ruthenium isomerisation product **7** forming the silylacetylene **8**,[17a] and a hydrido ruthenium complex **9**, which itself may also be catalytically active.

Obviously our ^{31}P-NMR experiment does not discount the possibility that very small concentrations of another class of ruthenium complex, which were not detectable by NMR, are mediating the reaction. Thus an alternative possibility is that decomposition of Grubbs' catalyst **3** generates a coordinatively unsaturated species **10** that then undergoes a more standard oxidative addition with the silane to generate an intermediate H–Ru–Si species **11** (Fig. 2).[17a] The thermal decomposition pathways of ruthenium alkylidene complexes have been investigated by Grubbs and proposed to

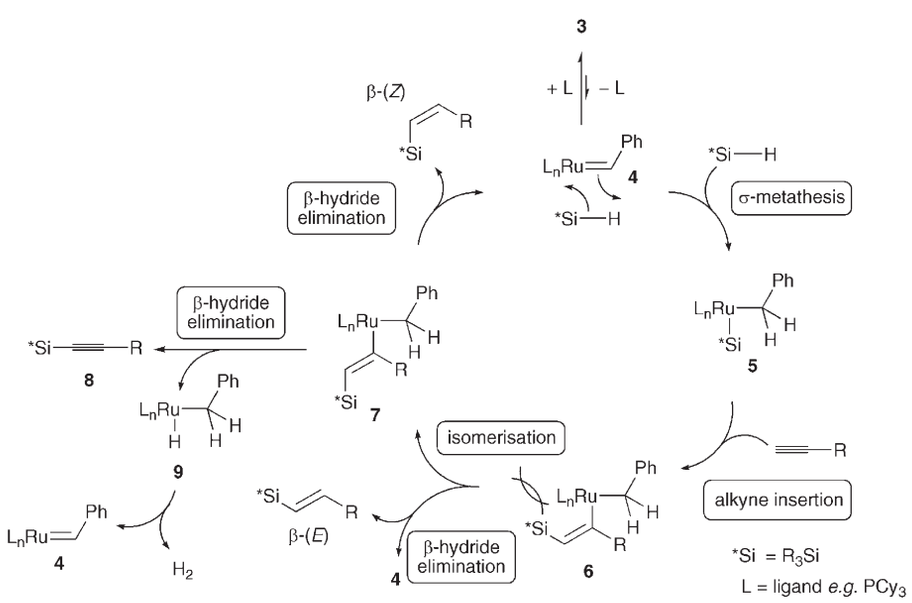

Fig. 1 A possible mechanism of hydrosilylation involving Grubbs' catalyst.

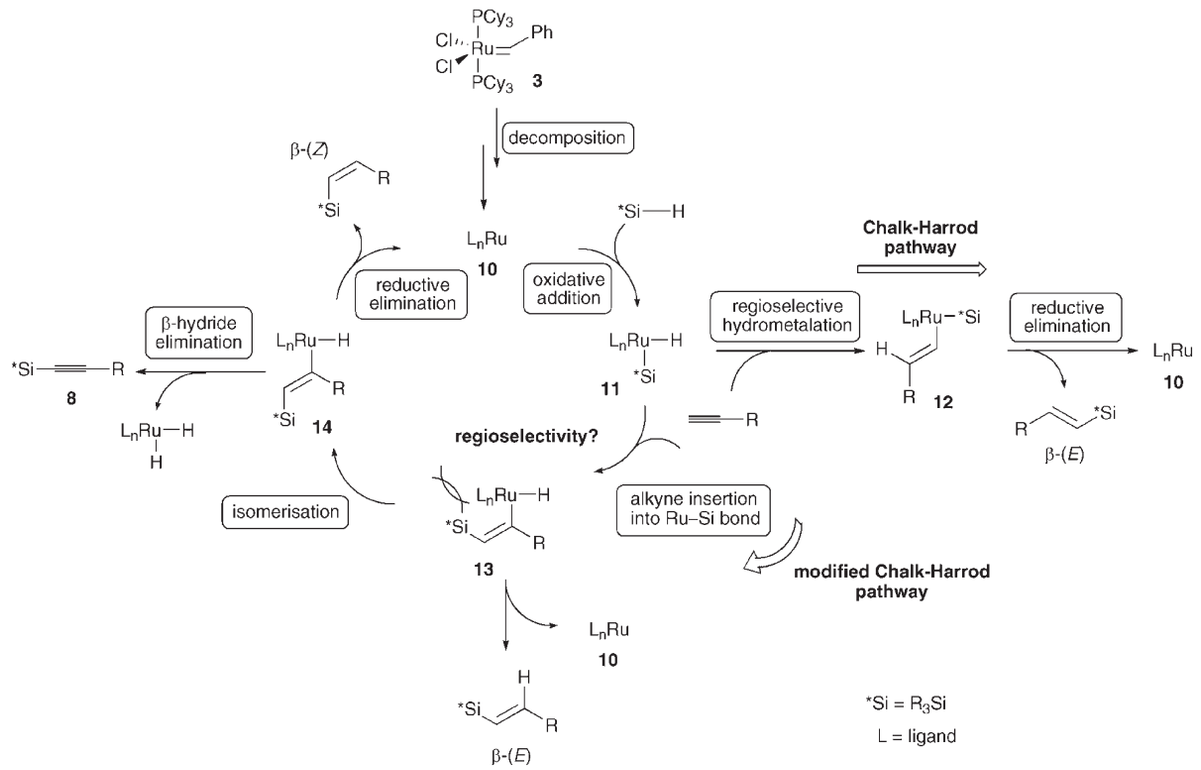

Fig. 2 Alternative mechanistic pathways could also account for the stereoselectivity of the hydrosilylation reaction.

involve initial phosphine dissociation (also required for metathesis) although the inorganic decomposition products have not been elucidated.[18] Furthermore the non-metathetic behaviour of Grubbs' catalyst **3**, for example in olefin isomerisation,[19] is often attributed to the formation of ruthenium hydride species through decomposition of the alkylidene pre-catalyst.[20] With a H–Ru–Si species **11** in hand, two possibilities for further reaction now exist. According to the classical Chalk–Harrod mechanism for hydrosilylation,[21] alkyne insertion into the Ru–H bond generates the vinyl ruthenium intermediate **12** through a net *syn* hydrometalation process in which the bulkier ruthenium centre adds to the less hindered alkyne terminus (in analogy to most hydrometalation reactions involving terminal alkynes). Subsequent reductive elimination would then afford the β-(*E*)-vinylsilane stereoisomer.[17a] However, since this isomer is only ever formed in trace quantities, with the exception of 3,3-dimethylbut-1-yne, the alternative pathway involving initial alkyne insertion into the Ru–Si bond should be considered as an alternative reaction pathway. In this case, and as before, regioselective *syn* addition of the Si–Ru bond across the alkyne provides a vinyl ruthenium complex **13**.[17a] Subsequent isomerisation to **14** as described above, followed by reductive elimination, would account for the formation of the β-(*Z*)-vinylsilane stereoisomer. This mechanism would also explain the formation of the silylacetylene by-product **8** in the same way as that outlined in Fig. 1.

The putative mechanisms described in Figs. 1 and 2 are stepwise in the way in which the silane and alkyne substrates react at the metal centre. A rather different mechanistic pathway for *cationic* ruthenium complexes has recently been proposed:[22] density functional calculations carried out by Trost suggested that oxidative addition of the Si–H bond to the ruthenium centre proceeds in a concerted fashion along with hydride insertion to the metal-activated alkyne. The calculations nicely accounted for the experimentally observed *anti* addition of the silane across the alkyne, as well as the observed Markovnikov addition regiochemistry.[9b] It may be the case that such a pathway is also be operating in our system although it is not clear how this mechanism would account for the differing regioselectivity obtained between Et_3SiH and $(EtO)_3SiH$. We believe this may be accounted for in another way. We have already suggested that terminal alkynes derived from propargyl alcohol provide the α-regioisomeric alkyne preferentially on account of the directing nature of the proximal oxygen substituent. In these cases, we suggest that direct *anti* metallametalation (as postulated by Trost)[22] of the longer (than Ru–H) Ru–Si bond across an alkyne coordinated to the Ru centre through the proximal oxygen donor group, would generate a relatively stable five-membered ruthenaoxacycle **15**, which on reductive elimination would provide the α-regioisomer (Fig. 3). Incorporating an additional methylene group between the oxygen donor and reacting alkyne functionality returns the selectivity in favour of the β-regioisomer (Table 2, entries 8 and 9) on account of i) the reduced stability of the analogous six-ring ruthenaoxacycle that would be formed in the 6-*endo* cyclisation mode;[23] ii) the availability of a more favourable 5-*exo* cyclisation mode; iii) location of the bulkier silyl substituent at the less hindered terminus of the alkyne (Fig. 3).

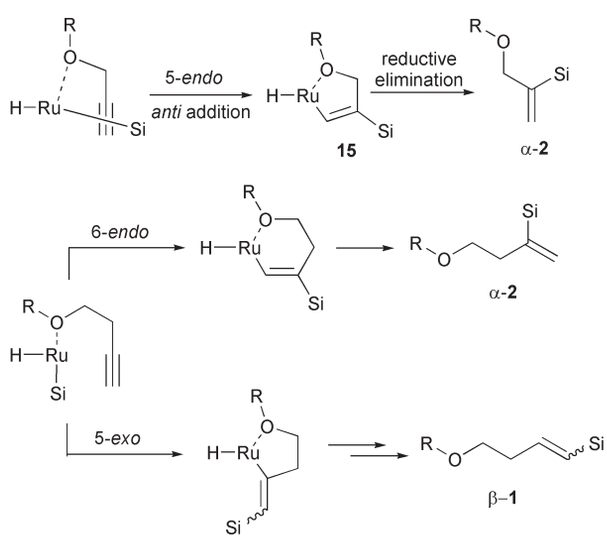

Fig. 3 Proximal donor groups affect the regioselectivity of hydrosilylation.

In the case of $(EtO)_3SiH$, which favours the α-regioisomer irrespective of whether or not a directing group is present in the alkyne substrate (Table 2, entries 17–22), we tentatively suggest that an oxygen atom in one of the ethoxy ligands on the silane provides a similar coordinating effect (Fig. 4). In this case, alkyne

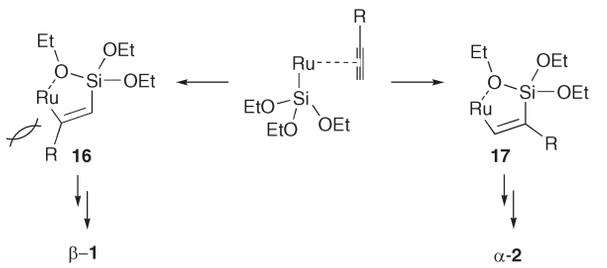

Fig. 4 Coordinating groups on the silane may also govern the regioselectivity of hydrosilylation.

insertion into the Ru–Si bond gives rise to two five-membered ruthenaoxasilacycle products **16** and **17** depending on the regioselectivity of insertion; since that (**16**) leading to the β-regioisomer suffers from unfavourable steric interactions between the ligands at the ruthenium centre and the alkyne substituent, a more favourable pathway *via* **17** is followed thereby accounting for the preferential formation of the α-regioisomer with this silane.

In summary, we have shown that commercially available Grubbs' first-generation metathesis catalyst can be used to mediate the hydrosilylation of terminal alkynes. In no case did we observe the presence of cross-metathesis products on analysis of the crude reaction mixture by GC-MS. The reaction selectivity displays an interesting reaction concentration dependence and more significantly, the choice of silane governs the regioselectivity. Although we have speculated upon possible mechanisms for this hydrosilylation, future work now needs to be directed towards validating these mechanistic hypotheses. Deuterium labelling studies, a thorough kinetics analysis of the reaction, and detailed NMR experiments, in addition to the identification of side-products by careful GC-MS analysis of the reaction mixture, will help shed light on our postulated mechanisms and allow us to identify favoured pathways. The commercial availability of Grubbs' catalyst **3**, and a number of related ruthenium alkylidene complexes, combined with their ease of handling, bodes well for the widespread uptake of these reagents for effecting hydrosilylation reactions. To this end, we now need to screen other metal alkylidene catalysts for hydrosilylation activity and further investigate the synthetic scope of the reaction by investigating other alkynes (including internal alkynes) and silanes.

Experimental

General procedure for hydrosilylation

Grubbs' catalyst **3** (2.5 or 5 mol%) was added in one portion to a solution of the alkyne (1.0 equiv.) and the silane (1.2 equiv.) in toluene (1 M or 0.1 M) and the reaction mixture was heated at 40 °C. TLC monitoring indicated that the reactions were generally complete within 10 h. Removal of the solvent under reduced pressure and purification by silica gel chromatography (hexane–Et_2O eluent) afforded the desired mixture of vinylsilane products as a colourless oil. No attempts were made to separate the isomeric mixtures.

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