Insertion of Vinylsilane into the Ruthenium–Silicon Bond—Direct Evidence for the Non-metallacarbene Mechanism of Silylalkene Disproportionation

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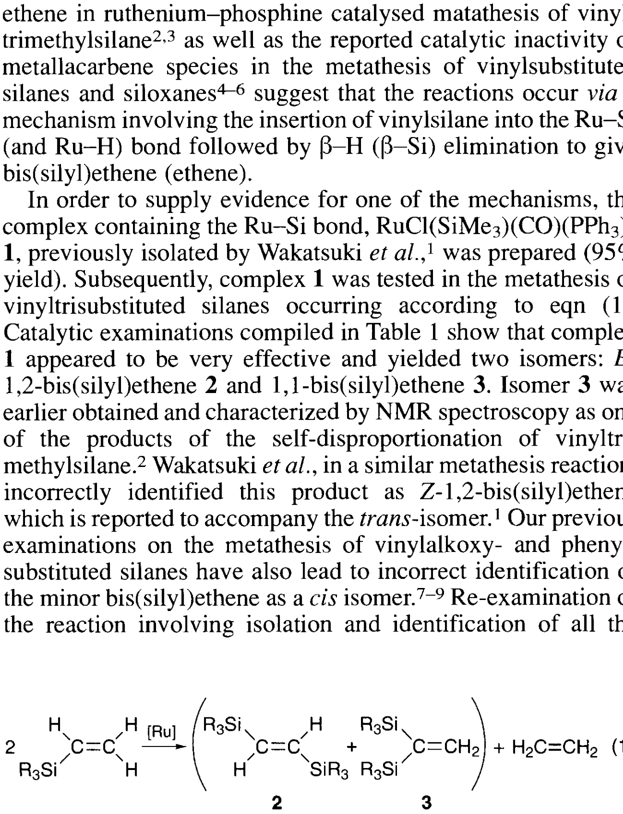
The reversible insertion of the vinylsilane molecule into the Ru–Si bond occurs in two different ways to give *E*-1,2-bis(silyl)ethene and 1,1-bis(silyl)ethene which, in combination with the previous experiments by Wakatsuki *et al.*, provides convincing evidence for a non-metallacarbene mechanism of silylalkene disproportionation.

Recent reports on the insertion of ethylene into the Ru–Si bond,[1] the formation of 1,1-bis(silyl)ethene beside *E*-1,2-bis(silyl)ethene in ruthenium–phosphine catalysed matathesis of vinyltrimethylsilane[2,3] as well as the reported catalytic inactivity of metallacarbene species in the metathesis of vinylsubstituted silanes and siloxanes[4–6] suggest that the reactions occur *via* a mechanism involving the insertion of vinylsilane into the Ru–Si (and Ru–H) bond followed by β–H (β–Si) elimination to give bis(silyl)ethene (ethene).

In order to supply evidence for one of the mechanisms, the complex containing the Ru–Si bond, RuCl(SiMe$_3$)(CO)(PPh$_3$)$_2$ **1**, previously isolated by Wakatsuki *et al.*,[1] was prepared (95% yield). Subsequently, complex **1** was tested in the metathesis of vinyltrisubstituted silanes occurring according to eqn (1). Catalytic examinations compiled in Table 1 show that complex **1** appeared to be very effective and yielded two isomers: *E*-1,2-bis(silyl)ethene **2** and 1,1-bis(silyl)ethene **3**. Isomer **3** was earlier obtained and characterized by NMR spectroscopy as one of the products of the self-disproportionation of vinyltrimethylsilane.[2] Wakatsuki *et al.*, in a similar metathesis reaction, incorrectly identified this product as *Z*-1,2-bis(silyl)ethene which is reported to accompany the *trans*-isomer.[1] Our previous examinations on the metathesis of vinylalkoxy- and phenyl-substituted silanes have also lead to incorrect identification of the minor bis(silyl)ethene as a *cis* isomer.[7–9] Re-examination of the reaction involving isolation and identification of all the products enables us to conclude that 1,1-bis(silyl)ethene is formed in the metathesis of all vinyltrisubstituted silanes. In ADMET (acyclic diene metathesis) polymerization of divinyltetramethyldisiloxane, oligomers formed during the reaction also contain the ≡Si–C(=CH$_2$)–Si≡ sequence showing the same scheme for their synthesis.[10]



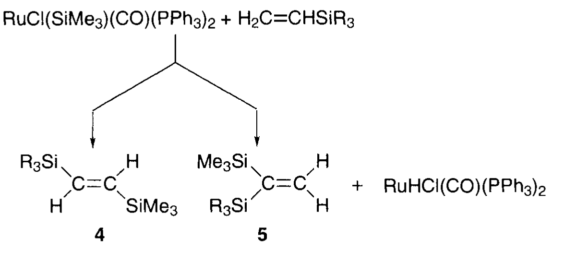
(1)

R$_3$ = Me$_3$, Me$_2$Ph, (OEt)$_3$

Table 1 Disproportionation of vinylsilanes catalysed by RuCl(SiMe$_3$)(CO)(PPh$_3$)$_2$–C$_6$H$_6$[a]

R$_3$	Conversion of H$_2$C=CHSiR$_3$ (%)	Yield of products (%) 2	3	2:3	Other
Me$_3$	85	50	30	1.7:1	trace
(OEt)$_3$	80	65	20	3.2:1	4
Me$_2$Ph	92	55	32	1.7:1	trace

[a] *Conditions*: 130 °C, 48 h, [Ru]:[H$_2$C=CHSi≡]:[C$_6$H$_6$] = 1:100:160, argon.



(2)

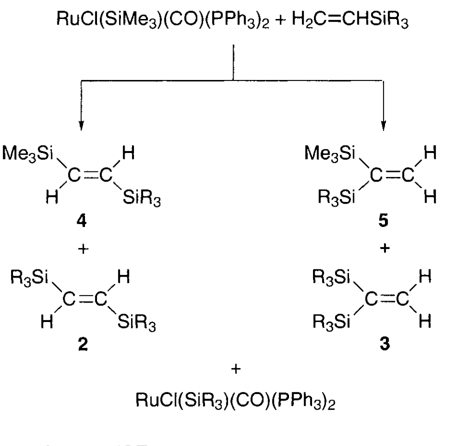
The reversible insertion of ethylene into an Ru–Si bond reported by Wakatsuki *et al.*[1] explains half of the catalytic cycle for metathesis of vinyltrisubstituted silanes. In order to produce evidence for the second half, it is necessary to perform experimentally insertion of the vinylsilane molecule into the Ru–Si bond [to yield finally bis(silyl)ethenes] and then test this process for its reversibility.

Therefore, the stoichiometric reaction of equimolar amounts of complex **1** with vinylsilane H$_2$C=CHSiR$_3$ was carried out to yield the products (identified by NMR spectroscopy and GC–MS) according to eqn (2).† The results are compiled in Table 2. Unfortunately, spectroscopic examinations did not confirm formation of RuHCl(CO)(PPh$_3$)$_2$ but, instead, proved the presence of the mixture of ruthenium silyl complexes which, presumably is due to high activity of the Ru–H bond with vinylsilanes. An excess of vinylsilane relative to **1** (3:1) allowed us to follow both the stoichiometric **4**, **5** and catalytic **2**, **3** reactions occurring according to Scheme 1. The reactions were examined at two temperatures (60 and 130 °C; see Table

Table 2 The reaction of RuCl(SiMe$_3$)(CO)(PPh$_3$)$_2$ **1** with vinylsilanes

R$_3$	[Ru]:[H$_2$C=CHSiR$_3$]	Conversion of H$_2$C=CHSiR$_3$ (%)	Yield of products (%) 4	5	2	3
(EtO)$_3$[a]	1:1	65	35	15	—	—
(EtO)$_3$[a]	1:3	85	23	16	12	20
(EtO)$_3$[b]	1:3	72	35	4	15	15
Me$_2$Ph[a]	1:1	45	18	4	—	—
Me$_2$Ph[a]	1:3	80	15	5	32	7
Me$_2$Ph[b]	1:3	65	13	2	24	5

[a] *Conditions*: 130 °C, 24 h. [b] *Conditions*: 60 °C, 24 h.



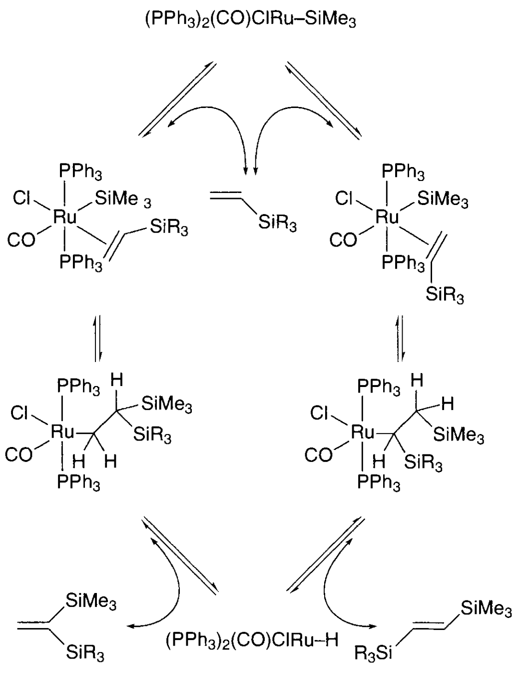
R$_3$ = Me$_2$Ph, (OEt)$_3$

Scheme 1

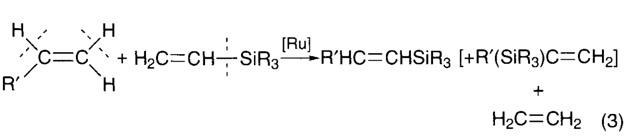
2). For R = OEt, the complex RuCl{Si(OEt)$_3$}(CO)(PPh$_3$)$_2$ was isolated and identified. The above experiments, for the first time, have allowed us to provide evidence for insertion of vinylsilane into the Ru–Si bond (or migration of silyl ligands) occurring *via* two ways to give two isomers according to Scheme 2.

Additional experiments involving the reaction of RuHCl(CO)(PPh$_3$)$_3$ with *E*-1,2-bis(silyl)ethene (130 °C, 24 h, Ar) enabled us to show the reversibility of the insertion process [7% of CH$_2$=CHSiR$_3$ and RuCl(SiMe$_3$)(CO)(PPh$_3$)$_2$ were detected] which is contrary to Wakatsuki's suggestions.[1]

Recent X-ray crystal structure determinations of five-coordinate complexes of the formula RuCl(SiR$_3$)(CO)(PPh$_3$)$_2$ (R = Et, OEt) revealed an approximately square-pyramidal geometry, with the silyl ligand apical and the triphenylphosphine ligands arranged mutually *trans*,[11] whereas Wakatsuki *et al.* had proposed a trigonal-bipyramidal geometry. Nevertheless, after coordination of vinylsilane, octahedral ruthenium complexes can finally be formed, in which the *cis* position of the Ru–SiR$_3$ bond to π-bonded vinylsilane is necessary for the observed insertion.



Scheme 2 Insertion of vinylsilane into Ru–Si bond



(3)

In conclusion, evidence for the first insertion of vinylsilane into a Ru–Si bond (and/or migration of the silyl ligand to vinylsilane bonded to the ruthenium complex), yielding two [*E*-1,2- and 1,1-bis(silyl)ethene] isomers has been presented. Together with the Wakatsuki's experiment, the results show that in the 'metathesis' of vinylsilanes and their 'co-metathesis' with alkenes, instead of C=C bond cleavage (formally characterizing alkene metathesis) a new type of the alkene conversion has actually been revealed, namely, dehydrogenative silylation of alkenes by vinylsilane, eqn. (3), where R′=SiR$_3$,[2,3,7,8] alkyl[9,12] or Ph.[12] This process occurs by C$_{\text{vinyl}}$–Si and C$_{\text{vinyl}}$–H bond cleavage.

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Footnotes

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† Full characterisation will be published as part of a forthcoming paper.

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