Ruthenium-catalyzed ring-closing reaction of α,ω-bis(vinylsilyl) compounds *via* a silyl transfer mechanism

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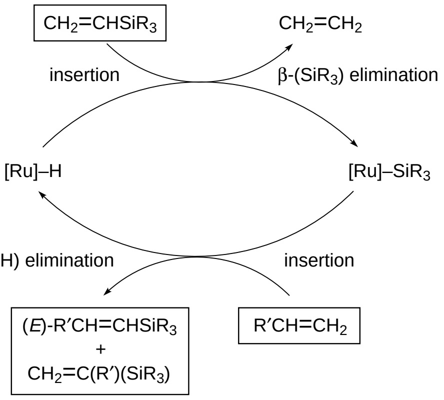
Compounds having a vinyldimethylsilyl group at both terminals have been successfully cyclized by ruthenium hydride catalysts to give selectively disilacycles of various ring sizes *via* a metathetical reaction, *i.e.* ethene elimination from the two terminal vinyl groups, not involving metallocarbene–metallacyclobutane type intermediates.

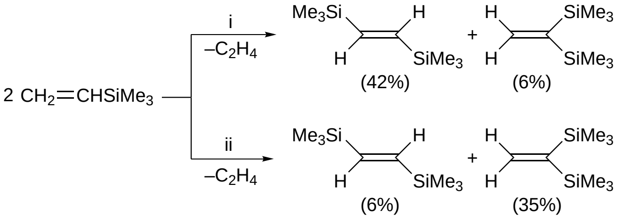
In 1991 we reported ruthenium hydride catalyzed homo- and cross-disproportionation reactions between $\mathrm{CH_2{=}CH\text{-}SiR_3}$ and $\mathrm{CH_2{=}CHR'}$ (R′ = $\mathrm{SiR_3}$, Me, Ph, $\mathrm{CO_2Me}$, $\mathrm{OBu^n}$) to yield $\mathrm{CH_2{=}CH_2}$ and $\mathrm{R'CH{=}CHSiR_3}$.[1] When R = Me and R′ = $\mathrm{SiMe_3}$ (homo-disproportionation), one of the disubstituted products originally assigned as the (*Z*)-isomer was subsequently identified by Marciniec and Pietrasuk as 1,1-bis(silyl)ethene.[2] We have also confirmed by NMR studies that in the case of cross disproportionations, *e.g.* R = R′ = Me, a minor product originally referred to as the (*Z*)-isomer is actually the 1,1-isomer. As a result, the catalytic sequence is now written as outlined in Scheme 1.



Scheme 1

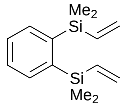
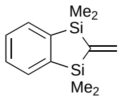
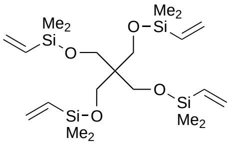
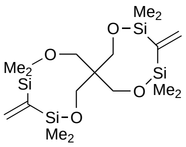
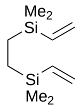
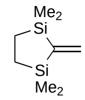
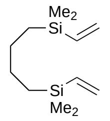
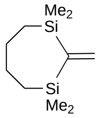
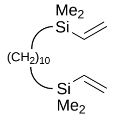
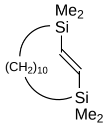
The reaction mechanism involving β-silyl elimination and insertion of a C=C double bond into the resulting Ru–Si bond was established in the original report based on isolation of the ruthenium–silyl intermediate $\mathrm{[RuCl(CO)(PPh_3)_2(SiMe_3)]}$ and its reaction with ethene.[1] This mechanism has been reconfirmed by a series of elaborate experiments by Marciniec and co-workers, who pointed out the possibility of involvement of metallocarbene and metallacyclobutane intermediates.[2–5] A remaining problem is that the regioselectivity of this reaction is poor in some cases, particularly for self-disproportionation-type reactions, where almost equal amounts of (*E*)-$\mathrm{R_3SiCH{=}CHSiR_3}$ and $\mathrm{CH_2{=}C(SiR_3)_2}$ are formed.[1] Apparently, the regioselection is controlled simply by the direction of insertion of the second olefin molecule into the Ru–Si bond.

Our efforts to improve the regioselectivity of the self-disproportionation of vinyltrimethylsilane, by modifying the electronic character and bulkiness of the ligands or by using coordinating additives, met with only partial success, yielding the (*E*)-1,2- and 1,1-isomers in an 88 : 12 ratio in one case and a 15 : 85 ratio at the other extreme (Scheme 2). The catalyst precursor used in the former was $\mathrm{[RuCl(CNC_6H_4\text{-}NO_2)(PPh_3)_3(H)]}$ while in the latter case, a small amount of MeCN was added to the initial reaction mixture containing $\mathrm{[RuCl(CO)(PPh_3)_3(H)]}$: without MeCN, the isomer ratio was 44 : 56.



Scheme 2 *Reagents and conditions*: i, $\mathrm{[RuCl(PPh_3)_3(CNC_6H_4\text{-}4\text{-}NO_2)(H)]}$ (20 mg), vinylsilane (0.2 ml), toluene (2 ml), 100 °C, 20 h; ii, $\mathrm{[RuCl(PPh_3)_3(CO)(H)]}$ (20 mg), MeCN (0.1 ml), vinylsilane (0.2 ml), toluene (2 ml), 100 °C, 20 h. GLC yields in parentheses.

Table 1 Disproportionation of α,ω-bis(vinylsilyl) compounds

Entry, Catalyst[a]	Substrate	Product	Yield (%)
1[b], A	 **1**	 **2**	87[c]
2[d], A	 **3**	 **4**	75[e]
3[f], B	 **5**	 **6**	83[c]
4[g], A	 **7**	 **8**	97[c]
5[h], B	 **9**	 **10**	76[e]

[a] A: $\mathrm{[RuCl(CO)(PPh_3)_3(H)]}$, B: $\mathrm{[RuCl(CO)(PPr^i{}_3)_2(H)]}$. [b] 80 °C, 24 h, toluene. [c] GLC yield. [d] 100 °C, 15 h, THF. [e] Isolated yield. [f] 60 °C, 24 h, THF. [g] 80 °C, 25 h, toluene. [h] 110 °C, 42 h, toluene.

Application of this catalytic system for intramolecular disproportionation of α,ω-bis(vinylsilyl) compounds was found to be more successful, giving disilacycles of various ring sizes: in particular, the regioselectivity was almost perfect (Table 1).‡ Only very small amounts of intermolecular reaction products was formed at normal concentrations of the reaction mixture, as detected by GC–MS, and they could be easily separated. By using either [RuCl(CO)(PPh_3)$_3$(H)] or Werner's hydride [RuCl(CO)(PPr^i_3)$_2$(H)] as the catalyst precursor,[6] the cyclic compounds with an *exo*-methylene unit were obtained as the sole cyclization products (Table 1, entries 1–4); the existence of the methylene unit in the products was confirmed by NMR DEPT studies. In contrast, a product which corresponds to the (*E*)-isomer, *i.e.* a 14-membered disilacycloolefin, was obtained selectively when the substrate had a longer aliphatic chain spacer (entry 5).§ In all of the cases examined, no isomeric material could be detected. Werner's hydride is in general more active as catalyst than the PPh_3 analog, but separation of the product from the catalyst and its residues is easier for the latter due to its low solubility.

The products in entries 1–4 correspond to the 1,1-isomer depicted in Scheme 2 and should not be formed in principle by the Grubbs type ring-closing metathesis using ruthenium–carbene initiators.[7] Obviously, the insertion–β-elimination mechanism shown in Scheme 1, is operating in an intramolecular fashion.

Further application of this novel ring-closing reaction to the synthesis of mono- and di-silamacrocycles, as well as to silicone-containing polymers, is now under investigation.

Notes and References

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‡ All new compounds gave satisfactory microanalytical data and mass spectra. *Selected data* for **2**: δ_H (270 MHz, $CDCl_3$) 6.53 (=CH_2); δ_C 154.2 (C=), 140.9 (=CH_2). For **4**: δ_H 6.33 (=CH_2); δ_C 154.2 (C=), 142.8 (=CH_2). For **6**: δ_H 6.37 (=CH_2); δ_C 156.5 (C=), 138.4 (=CH_2). For **8**: δ_H 6.28 (=CH_2); δ_H 155.4 (C=), 139.4 (=CH_2). For **10**: δ_H 6.53 (HC=CH); δ_C 150.4 (HC=CH).

§ The (*E*)-confuguration of **10** was confirmed by preparing the product by another route, *i.e.* the reaction of (*E*)-$Me_2ClSiCH{=}CHSiClMe_2$ with $BrMg(CH_2)_{10}MgBr$ under diluted conditions. This route, however, also gives by-products.

1 Y. Wakatsuki, H. Yamazaki, M. Nakano and Y. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1991, 703.

2 B. Marciniec and C. Pietraszuk, *J. Chem. Soc., Chem. Commun.*, 1995, 2003.

3 B. Marciniec, Z. Foltynowicz, C. Pietraszuk, J. Gulínski and H. Maciejewski, *J. Mol. Catal.*, 1994, **90**, 213.

4 B. Marciniec, C. Pietraszuk and Z. Foltynowicz, *J. Organomet. Chem.*, 1994, **474**, 83.

5 B. Marciniec and C. Pietraszuk, *Organometallics*, 1997, **16**, 4320.

6 M. A. Esteruelas and H. Werner, *J. Organomet. Chem.*, 1986, **303**, 221.

7 For example, see P. Schwab, M. B. France, J. W. Ziller and R. H. Grubbs, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2039. For a recent review on olefin metathesis, see M. Schuster and S. Blechert, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2037.

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