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Cyclohydrosilylation dimer formation: evidence for $Pt^0 \leftrightarrow Pt^{II} \leftrightarrow Pt^{IV}$ catalysis *, **

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Abstract

An eight-membered cyclic compound, 2,2,3,4,4,6,6,7,8,8-decamethyl-1,5-dioxa-2,4-disilacyclooctane (VIII), along with the expected five-membered 2,2,5,5-tetramethyl-1-oxa-2-silacyclopentane (V) were found to be the major products when vinyldimethylcarbinoxydimethylsilane (I) (*i.e.* 2-methyl-3-buten-2-oxydimethylsilane) was subjected to cyclohydrosilylation using platinum catalysis. The eight-membered product (VIII) readily undergoes β-elimination during gas chromatography (GC) analysis to extrude 2-methyl-2-butene giving the six-membered 2,2,4,4,5,6,6-heptamethyl-1,3-dioxa-2,4-disilacyclohexane (VI). Contrary to an earlier report (T.H. Lane and C.L. Frye, *J. Organomet. Chem.*, *172* (1979) 213), no siloxetane or silanone intermediates are needed to rationalize the formation of the six-membered cyclic compound. When (Wilkinson's) rhodium catalyst was used for the hydrosilylation, only V was formed. The formation of VIII with platinum catalysis is rationalized by a mechanism utilizing successive oxidative additions to both Pt^0 and Pt^{II} catalytic species; *i.e.* the absence of a second catalytically active level of rhodium is believed responsible for its inability to yield the eight-membered cyclic. Similarly, dimerization of either 1,1-dimethyl-1-silacyclobutane or 1,1,3,3-tetramethyl-1,3-disilacyclobutane to form the cyclooctanes can be readily achieved by platinum catalysis but not by rhodium catalysis. These results constitute the first examples of processes believed to require the presence of not only one but two catalytically active oxidation levels.

1. Introduction

Cyclohydrosilylation (intramolecular hydrosilylation) has gained acceptance as a powerful tool for certain selective organic syntheses in recent years. For example, cyclohydrosilylation of allyl alcohols has been used extensively in the stereoselective synthesis of 1,3-diols [1–3]. Cyclohydrosilylation of allylamines has been similarly used for the stereoselective synthesis of amino alcohols [4]. In this last report, a four-membered 1-aza-2-silacyclobutane, surprisingly, was reported to be the initially isolated product from cyclohydrosilylation. Earlier, one of us (C.L.F.) in a study of the cyclohydrosilylation of vinyldimethylcarbinoxydimethylsilane (I) had postulated the formation of the then hypothetical four-membered siloxetane (IV) along with the expected five-membered silacyclopentane (V). The siloxetane was not isolated but was postulated to eliminate dimethylsilanone under very mild conditions. The postulated dimethylsilanone and the siloxetane could then give the observed six-membered 2,2,4,4,5,6,6-heptamethyl-1,3-dioxa-2,4-disilacyclohexane (VI) as shown [5] in Scheme 1.

Although stable four-membered siloxetanes have since been isolated [6], all were decorated with bulky groups to stabilize the ring. A simple siloxetane, such as IV, has never been isolated at ambient conditions. Previous attempts to prepare such simple siloxetanes have sometimes led to the formation of products suggestive of dimethylsilanone intermediacy [7]. While the siloxetane structure is strained, the isolation of siloxetane IV was not thought to be prohibitively difficult. Thus it was hoped that if cyclohydrosilylation of I were to be performed under sufficiently mild conditions, siloxetane IV might be stable enough to allow isolation. We therefore decided to re-examine the cyclohydrosilylation of vinyldimethylcarbinoxydimethylsilane (I), hoping to isolate the simple siloxetane for use as a dimeth-

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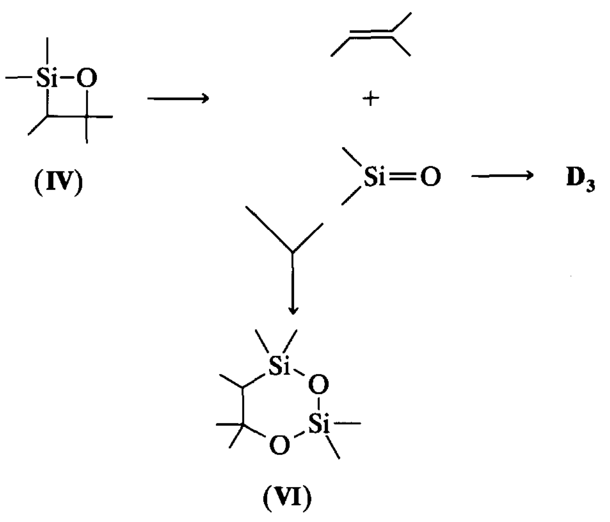

Scheme 1.

ylsilanone generator under relatively mild conditions. As shown below, however, we obtained results which have forced us to abandon the notion that siloxetane and silanone intermediates are involved in these cyclohydrosilylation reactions and to propose a novel mechanistic pathway requiring the sequential involvement of two catalytically active platinum oxidation levels.

2. Results and discussion

2.1. Cyclohydrosilylation of vinyldimethylcarbinoxydimethylsilane

Our cyclohydrosilylation reactions of **I** were typically run in 5–10% pentane solutions using a divinyltetramethyldisiloxane stabilized soluble platinum catalyst. High dilution with pentane was used for two purposes: (i) to dissipate the heat generated from the expected exothermic hydrosilylation reaction in order to avoid thermolysis of any siloxetane formed; (ii) to eliminate or minimize the formulation of polymers from intermolecular hydrosilylation reactions. Divinyltetramethyldisiloxane stabilized platinum catalyst was used at a silane to platinum ratio of approximately 1000 : 1. These high catalyst levels resulted in cyclohydrosilylation proceeding smoothly at room temperature without the sudden vigorous exotherms often observed with chloroplatinic acid. Reaction progress was monitored by the disappearance of **I** by GC.

Although this platinum catalyzed cyclohydrosilylation of **I** gave somewhat complicated GC traces, there were generally two particularly prominent product peaks. GC-MS analysis of these two products showed them to be the expected five-membered 2,2,5,5-tetramethyl-1-oxa-2-silacyclopentane (**V**) and the previously reported [5] six-membered 2,2,4,4,5,6,6-heptamethyl-1,3-dioxa-2,4-disilacyclohexane (**VI**). Consistently missing, however, was the previously reported [5] hexamethylcyclotrisiloxane (**D_3**). More interestingly, however, the GC peaks for **V** and **VI** were observed only when using platinum catalysts (either divinyltetramethyldisiloxane complexed platinum or chloroplatinic acid). With rhodium catalysts [tris(triphenylphosphine)rhodium chloride or rhodium trichloride], no **VI** was observed although **V** was present.

We then observed that vacuum stripping of the platinum catalyzed reaction mixture, at room temperature to remove the solvent and the silacyclopentane **V** afforded a low melting solid. Recrystallization of this low melting solid was achieved at sub-ambient temperature using pentane. This crystalline solid undergoes facile thermal decomposition to give 2-methyl-2-butene and the six-membered disilacyclohexane **VI**. Previously, during GC monitoring of the cyclohydrosilylation, 2-methyl-2-butene had been overlooked since it co-eluted with the solvent.

The proton NMR spectrum of this thermally unstable crystalline material showed four kinds of absorptions. Those at δ 0.05 (s, 3H) and δ 0.10 (s, 3H) were assigned to the methyl groups attached to silicon. The absorption at δ 1.25 (s, 6H) was assigned to the $C(CH_3)_2$ group. The absorptions at δ 0.5–1.0 (m, 4H) lacked A_2B_2 symmetry expected for products of the normal hydrosilylation reactions that would result in $-SiCH_2CH_2-$ linkages and is therefore assigned to the $-Si(CH_3)CH-$ moiety that results from the non-terminal addition which would result in complicated AB_3 NMR patterns.

Although the above NMR data were not incompatible with the four-membered siloxetane structure for this crystalline compound, its vapor pressure was clearly much too low for that to be true. Chemical ionization mass spectroscopy of this crystalline compound using ammonia as the reagent gas clearly established its molecular weight to be 288, *i.e.* a dimer of the supposed siloxetane. An eight-membered ring structure, 2,2,3,4,4,6,6,7,8,8-decamethyl-1,5-dioxa-2,6-disilacyclooctane (**VIII**), was assigned to this solid [8*] based on the above information. Thus, cyclohydrosilylation of **I** gives both **V** and **VIII** as major products, and the latter decomposes upon heating [9*] to generate 2-methyl-2-butene and **VI** as shown below in Scheme 2.

Similarly, cyclohydrosilylation of vinyldimethylcarbinoxymethylphenylsilane (**I–A**) and vinyldimethyl-

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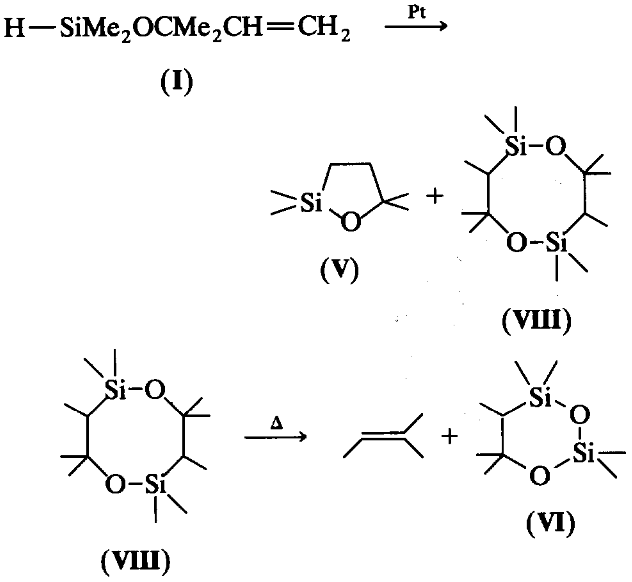
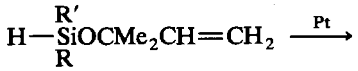
* Reference number with asterisk indicates a note in the list of references.

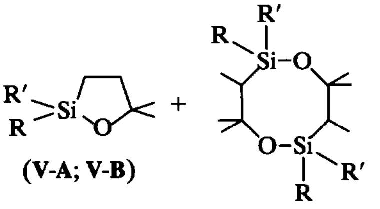


Scheme 2.

carbinoxydiphenylsilane (I–B) yielded the five- and eight-membered cyclics as shown below:


$$H\!-\!\underset{R}{\overset{R'}{Si}}OCMe_2CH\!=\!CH_2 \xrightarrow{Pt}$$

(I-A: R = Me R′ = Ph;
I-B: R = R′ = Ph)

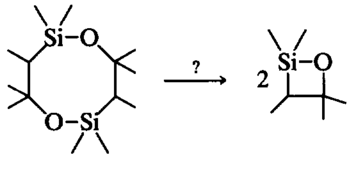


(V-A; V-B)

(VIII-A; VIII-B)

2.2. *Pyrolysis of 2,2,3,4,4,6,6,7,8,8-decamethyl-1,3-dioxa-2,4-disilacyclooctane as a possible silanone generator*

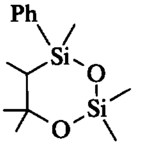
Although the above results established that siloxetane was not formed under ambient conditions, there was still the possibility that upon heating, disilacyclooctane VIII might actually be decomposing to afford the elusive siloxetane. The resulting siloxetane would then extrude dimethylsilanone which could then insert into unreacted siloxetane as speculated previously and shown earlier in Scheme 1.



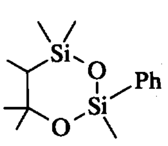
(VIII)

(IV)

To test this hypothesis, individual pyrolyses of VIII and VIII-A with 10-fold hexamethylcyclotrisiloxane (D_3) added as the silanone trap were studied. Should silanone be generated, trapping of the silanone should then have yielded the respective cyclotetrasiloxanes, octamethylcyclotetrasiloxane and phenylheptamethylcyclotetrasiloxane. However, only the respective six-membered disilacyclohexanes (VI and VI-A) and 2-methyl-2-butene were formed. The silanone trapped products were not formed in sufficient quantities to be detected, if at all. Co-pyrolysis of VIII and VIII-A was also studied. Should both siloxetane and silanone be generated, mixed six-membered cyclics such as VI-C and VI-D (see below) would be expected to be formed.



(VI-C)



(VI-D)

Again, the major products formed were VI and VI-A and 2-methyl-2-butene with no evidence for the formation of mixed cyclics. Thus it appears very unlikely that either siloxetane or silanone intermediates are involved in the decomposition of VIII, and that direct β-elimination [10] of olefin from VIII is occurring. Thermal instability of a similar 1,5-dioxa-2,6-disilacyclooctane has also been reported recently [11].

2.3. *Possible mechanism of the cyclohydrosilylation*

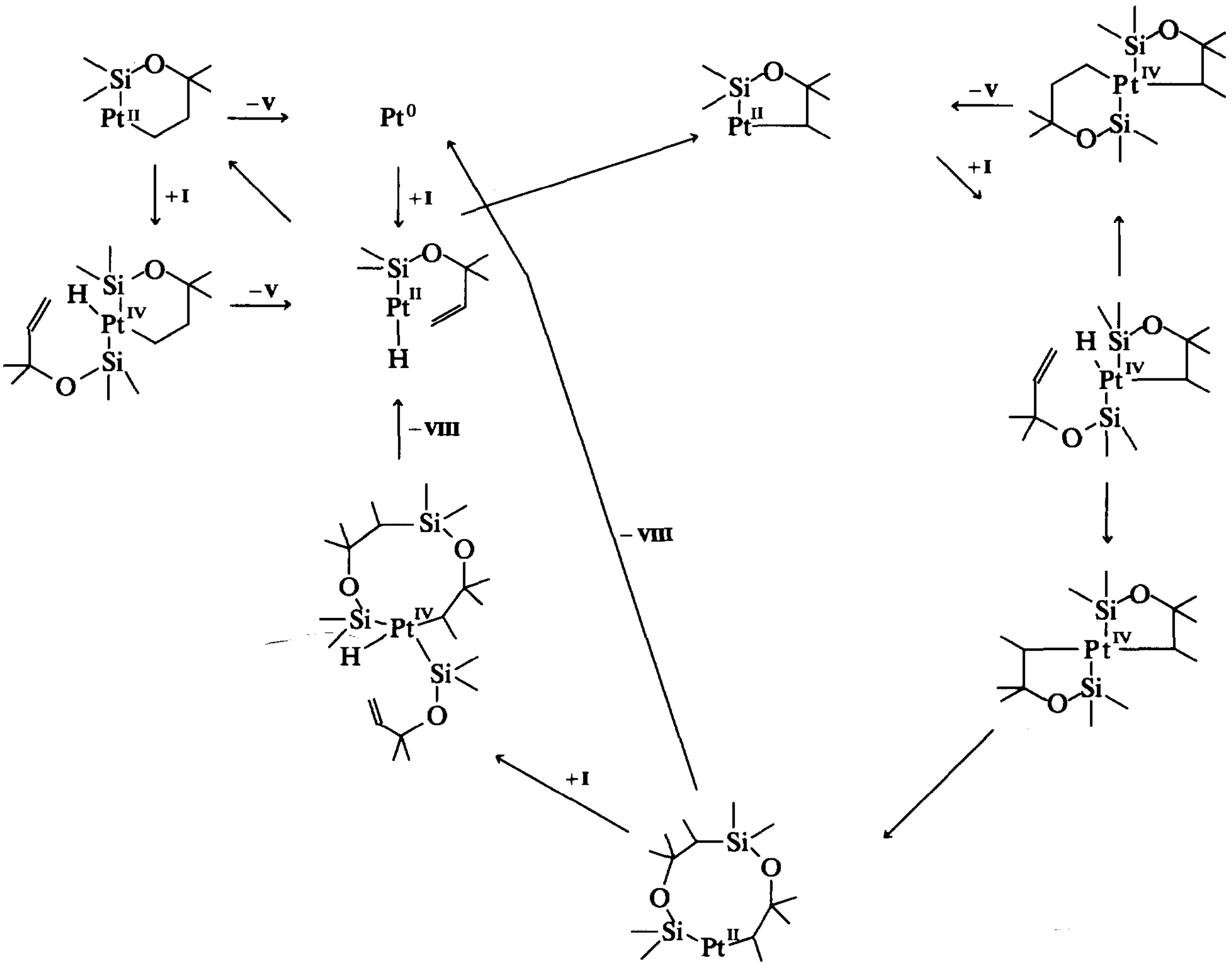
The mechanism of hydrosilylation has been the subject of numerous studies, and Harrod and Chalk's "oxidative addition" rationale [12] is widely accepted. In this mechanism, either Pt^0 or Pt^{II} can be considered the active species. An olefin–platinum complex formation before or after the oxidative addition of silane to platinum is thought to bring both the silane and olefin to the coordination sphere of platinum. Insertion of the olefin into the Pt–H bond followed by the reductive elimination of the hydrosilylated product can then regenerate the catalyst.

Harrod and Chalk's mechanism, with slight modification, can also adequately explain our present results. Scheme 3 below shows our attempt to account for the formation of both V and VIII. All the non-essential ligands were omitted from the diagram to keep the scheme simple and clear. Although our illustration shows the silane addition preceding the olefin–platinum complex formation, a similar mechanism can also be drawn with olefin–platinum complex formation preceding the addition of silane. While Harrod and Chalk's mechanism assumes the active catalyst to be either Pt^0 or Pt^{II}, our mechanism requires *both* Pt^0

and Pt^{II} to be catalytically active and to sequentially participate in the catalysis. In our mechanism, addition of vinyldimethylcarbinoxydimethylsilane (I) to Pt^0 yields five- or six-membered platinum(II) containing heterocyclics. The six-membered Pt^{II} heterocyclic can reductively eliminate the five-membered **V** owing to the stability of the five-membered product. The five-membered Pt^{II} heterocyclic, on the other hand, is postulated to be unable to undergo reductive elimination to give strained four-membered siloxetane. However, it can further react with another molecule of **I** to form either of two spirocyclic Pt^{IV} species. The spirocyclic Pt^{IV} compound that contains a six- and a five-membered ring would again rapidly reductively eliminate **V** owing to its stability. The spirocyclic compound containing two five-membered heterocyclics, on the other hand, can undergo a reductive elimination rearrangement to give a nine-membered Pt^{II} heterocyclic. The nine-membered Pt^{II} heterocyclic can either undergo reductive elimination to generate **VIII** and Pt^0 or further oxidatively add another molecule of **I** to form the nine-membered Pt^{IV} heterocyclic which could reductively eliminate the eight-membered **VIII** and regenerate the Pt^{II} complex of **I**.

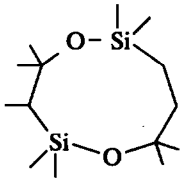
The above mechanism adequately explains the formation of **VIII**. To the best of our knowledge, it is the first example where both Pt^0 and Pt^{II} are required to explain the formation of a hydrosilylation product. With rhodium catalysis, successive oxidative additions and successive reductive eliminations cannot take place. Therefore, formation of **VIII** should be precluded with rhodium catalysis, as observed.

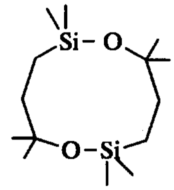
The above mechanism, however, does not prohibit the formation of either nine-membered or the ten-membered cyclics such as **IX** and **X**. It also does not prohibit the formation of head-to-head addition products such as **VIII′**. None of the three cyclic products, however, were identified in our present studies. In the former case, formation of **V** is evidently much more favorable than either the elimination of **IX** or **X**; *i.e.*

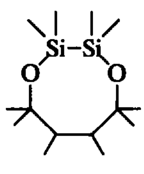


Scheme 3.

spirocyclic species that contain the six-membered Pt^{IV} heterocyclic eliminate V. Concerning the head-to-head addition product **VIII'**, **VIII** is probably thermodynamically more favored than **VIII'** owing to higher bond energy of the Si–C bond compared with that of the Si–Si bond (~ 89 *vs.* ~ 80 kcal mol^{-1}) [13].


(IX)

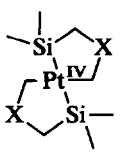

(X)


(VIII')

2.4. Platinum catalyzed dimerization of 1,1-dimethylsilacyclobutane and 1,1,3,3-tetramethyl-1,3-disilacyclobutane

Our present studies also showed that at high dilution, both 1,1-dimethyl-silacyclobutane and 1,1,3,3-tetramethyl-1,3-disilacyclobutane can be smoothly converted into their respective cyclic dimers using platinum catalysts, as judged by GC-MS. However, when reactions were run using rhodium catalysis, it was clear that none of the cyclic dimers were formed.

It is, of course, well-known that strained silacycles such as silacyclobutane and disilacyclobutane undergo polymerization reactions using platinum catalysis [14]. Kriner also studied the disilacyclobutane polymerization reaction and observed the formation of a small amount of the cyclic dimer [15] and proposed an ionic mechanism for the formation of the dimer. Cundy *et al.* also studied the reaction [16]. The rationalized the product formation by an initial oxidative addition of the silacycles to the transition metal followed by the formation of a linear transition metal–alkyl complex. Polymer growth can be achieved by insertion of another silacycle into the linear complex. Cyclic dimer formation was thought to be the result of ring closure of the linear complex. In our opinion, an ionic mechanism as suggested by Kriner is unlikely. Although Cundy's mechanism can adequately explain the formation of polymers, ring closure of the linear complex to give the cyclic dimer is not favored due to kinetic considerations. We suggest that oxidative addition of the silacycle to Pt^0 will generate a Pt^{II}-containing five-membered heterocycle which can then undergo further oxidative addition of another silacycle to give a Pt^{IV} complex such as the one shown below:



($X = CH_2, SiMe_2$)

Such complexes can then undergo reductive elimination to form nine-membered Pt^{II} heterocycles. Oxidative addition of another silacycle followed by reductive elimination of the cyclic dimer can then generate the active Pt^{II} heterocycle. Again, two successive oxidative additions are required to account for the formation of dimer. Rhodium catalysts, incapable of undergoing such successive oxidative additions, are therefore not expected to be active catalysts for the dimerization of either silacyclobutanes or disilacyclobutanes.

3. Conclusions

Our present studies have shown that cyclohydrosilylation of vinyldimethylcarbinoxydimethylsilane using platinum catalysis yields the expected five-membered V along with the unexpected eight-membered **VIII**. The eight-membered **VIII** was found to extrude 2-methyl-2-butene upon heating. No siloxetane intermediacy was observed during either formation of **VIII** or its subsequent decomposition. The formation of **VIII** appears to be unique for platinum catalysis; no **VIII** was formed when the reaction was run using rhodium catalysts. The difference was attributed to the ability of platinum to undergo successive oxidative additions due to the availability of three oxidation states (0, II and IV). As further support, it was shown that dimerizations of silacyclobutane and disilacyclobutane can also take place with platinum catalysts but not with rhodium catalysts. Successive oxidative additions to a transition metal could be a very common feature for transition metals having more than two common oxidation states. For example, the disilane metathesis reported by Tamao *et al.* [17] using palladium catalysis could also be adequately explained by a similar mechanism.

4. Experimental details

4.1. General

Gas liquid chromatography analysis employed a Hewlett-Packard Model 5840A gas chromatograph equipped with a 18835B capillary inlet system. Proton NMR spectra were recorded on a Varian A-60 using CCl_4 as the solvent and $CHCl_3$ as the internal standard. GC-MS spectra were obtained on a Hewlett-Packard 5992 GC/MS system equipped with a 18740B capillary inlet system.

Chloroplatinic acid and platinumdivinyltetramethyldisiloxane complex from Petrarch Systems were used. Tris(triphenylphosphine)rhodium(I) chloride (Wilkinson's catalyst) and rhodium trichloride were purchased from Aldrich Chemical Co. Milwaukee, WI.

Vinyldimethylcarbinoxydimethylsilane (I) was prepared according to the method described by Lane and

Frye [1]. Both 1,1-dimethylsilacyclobutane and 1,1,3,3-tetramethyl-1,3-disilacyclobutane were prepared as described elsewhere [14].

4.2. Cyclohydrosilylation of vinyldimethylcarbinoxydimethylsilane (I)

Typically, a three-necked round bottom flask was fitted with a reflux condenser and an addition funnel. A solution containing 0.02 mmol of platinum in 25 ml pentane was then placed in the flask. A solution of vinyldimethylcarbinoxydimethylsilane (I, 3.60 g; 0.025 mol) was then slowly added with the addition funnel while stirring magnetically. The mixture was maintained at room temperature and periodically monitored by GC. Two major product peaks were noted by GC, along with many minor products.

For preparative purposes, the above reaction was scaled up ten-fold. After the reaction was complete, the mixture was stripped at room temperature in vacuum with a cold trap to remove the volatiles. The trapped material then was fractionated on a 2′ spinning band distillation column to afford **V**. The ^{1}H NMR spectrum of **V** showed: δ 0.1 (s, 6H), δ 0.8 (t, 2H), δ 1.2 (s, 6H) and δ 1.8 (t, 2H). Mass spectroscopy showed fragments at 129 ($M-CH_3$) 101, 75 among others.

The reaction mixture remaining after stripping was a viscous oil or a semisolid. Recrystallization from pentane afforded white crystalline **VIII**, m.p. 75–76°C. The ^{1}H NMR spectrum showed: δ 0.05 (s, 3H), δ 0.10 (s, 3H), δ 0.5–1.0 (m, 4H) and δ 1.25 (s, 6H). Chemical ionization mass spectroscopy using ammonia as the reagent gas showed the following peaks: 323 ($M+N_2H_7^+$), 306 ($M+NH_4^+$), 289 ($M+H^+$) and lower mass peaks. The base peak had a mass of 70 (2-methyl-2-butene). Electron impact mass spectroscopy showed identical patterns to that of **VI** (shown later).

The total combined weight of **V** and **VIII** isolated accounted for more than 70% of the starting material, with roughly equal amounts of **V** and **VIII**. In contrast to the above hydrosilylation, when the reaction was run using Wilkinson's catalyst, GC analysis indicated only the formation of **V** along with many complex reaction products. No formation of **VIII** or **VI** was noted on GC.

4.3. Pyrolysis of 2,2,3,4,4,6,6,7,8,8-decamethyl-1,5-dioxa-2,6-disilacyclooctane (VIII)

During either GC analysis or heating to 200°C, the cyclic **VIII** decomposes to 2-methyl-2-butene and 2,2,4,4,5,6,6-heptamethyl-1,3-dioxa-2,4-disilacyclohexane **VI**. The identity of 2-methyl-2-butene was confirmed by comparing its NMR and MS characteristics with those of an authentic sample. The identity of **VI** was also confirmed by comparison of its NMR and MS spectral data with those of authentic material prepared previously and described elsewhere [5]. ^{1}H NMR: δ 0–0.2 (M, 12H), δ 0.7–1.0 (m, 4H) and δ 1.2 (s, 6H). Mass spectroscopy showed peaks at 203 ($M-CH_3$), 189, 149 (base peak) and 133 among other peaks.

4.4. Preparation of vinyldimethylcarbinoxyphenylmethylsilane (I-A)

Vinyldimethylcarbinoxyphenylmethylsilane was prepared by reacting phenylmethylchlorosilane with vinyldimethylcarbinol in pentane using pyridine as the acid acceptor. After the reaction was complete, as monitored by GC, the pyridine hydrochloride was removed by filtration; distillation at 73°C (2.5 mmHg) afforded **I-A** in 54% yield. ^{1}H NMR: δ 0–0.2 (m, 3H), δ 1.1 (broad s, 6H), δ 4.4–5.9 (m, 4H) and δ 6.8–7.4 (m, 5H). Mass spectroscopy showed peaks at 206 (M), 191 ($M-CH_3$) and 137 (base peak).

4.5. Preparation of vinyldimethylcarbinoxydiphenylsilane (I-B)

Diphenylsilane (48.00 g; 0.26 mol) and vinyldimethylcarbinol (21.50 g; 0.25 mol) were placed in a magnetically stirred 250 ml round bottom distillation flask with stirring. Tetrabutylammonium fluoride (0.10 g of 1 M solution in THF) was then added and the flask was immediately fitted with a distillation column. Evolution of H_2 from the reaction mixture was initially very vigorous but subsided in 30 min. The product **I-B** was vacuum distilled at 129°C (1.4 mmHg). Yield 60.99 g (94%). ^{1}H NMR: δ 1.4 (s, 6H), δ 4.8–6.2 (m, 4H) and δ 7.2–7.7 (m, 10H). Mass spectroscopy: 268 (M), 253 ($M-CH_3$), 199, 183 and 123 (base peak).

4.6. Cyclohydrosilylation of vinyldimethylcarbinoxyphenylmethylsilane (I-A)

Cyclohydrosilylation followed a procedure similar to that described above for **I**. After the reaction was complete, the mixture was vacuum stripped to remove pentane. The stripped product mixture (**V-A** and **VIII-A**) was a white solid. Washing of the solid with cold pentane dissolved most of **V-A**. No attempt was made to distill **V-A**. **V-A** was identified by GC/MS only. Its mass spectrum showed peaks at: 206 (M), 191 ($M-CH_3$, base peak) among other peaks. The white solid after pentane washing showed ^{1}H NMR absorption at δ 0.4 (s, 3H), δ 0.6–1.0 (m, 4H), δ 1.2 (d, 6H) and δ 7.0–7.6 (m, 5H). GC analysis of the white solid showed four peaks for **VI-A** and 2-methyl-2-butene. The four peaks are due to the four stereoisomers of **VI-A**. All four **VI-A** peaks showed identical mass spectroscopic fragmentation patterns at: 327 ($M-CH_3$), 273, 257, 251 and 195 (base peak) among other peaks.

4.7. Cyclohydrosilylation of vinyldimethylcarbinoxydiphenylsilane (I-B)

Cyclohydrosilylation of **I-B** was also performed by a procedure similar to that used with **I**. Shortly after the reaction, a white solid precipitate formed. It was sparingly soluble in chloroform, methylene chloride or benzene. GC analysis of the chloroform solution gave only 2-methyl-2-butene. The presumed decomposition product **VI-B** did not elute. The dilute $CDCl_3$ solution of this solid did not give well resolved ^1H NMR absorptions. Nevertheless, it showed absorptions at δ 0.8–1.2 (m, 7H), δ 1.3 (s, 3H) and δ 7.2–8.8 (m, 10H). The mother liquor showed only one GC peak other than the pentane solvent. MS analysis of this material suggested its identity of **V-B**: 268 (M), 253 ($M - CH_3$, base peak), 239, 212 among other peaks.

4.8. Pyrolyses of the 1,5-dioxa-2,6-disilacyclooctanes (VIII and VIII-A)

Pyrolysis of either **VIII** or **VIII-A** with a ten-fold excess of hexamethylcyclotrisiloxane was performed in a 3/8" heavy wall sealed tube at 250°C for 30 min. GC analysis of the resulting clear liquid showed the presence of 2-methyl-2-butene, hexamethylcyclotrisiloxane, and the six-membered products (**VI** or **VI-A** respectively). We were not able to identify all the minor products formed. Silanone trapped cyclotetrasiloxanes were formed in trace amounts if at all, providing no evidence for silanone generation under such conditions.

Similarly, co-pyrolysis of **VIII** and **VIII-A** was also carried out in sealed tubes with a 1:1 mixture of **VIII** and **VIII-A**. The solid mixture was heated to 250°C for 30 min. The resulting clear liquid after cooling was found to contain mainly 2-methyl-2-butene, **VI** and **VI-A**. Although we were unable to detect all the minor products and determine their structures, mixed six membered ring products such as **VI-C** or **VI-D** were at most formed in trace quantities, if at all. Again, no evidence for silanone intermediate was found.

4.9. Platinum catalyzed dimerization of 1,1-dimethyl-1-silacyclobutane

Enough pentane solution of a divinyltetramethyldisiloxane stabilized platinum catalyst was added to a solution of 1,1-dimethyl-1-silacyclobutane (0.50 g; 5 mmol) in 10 g pentane to give the platinum/silicon ratio of approximately 1/1000. The mixture was heated under reflux for 30 min. GC analysis of the solution indicated the formation of a major product shown by GC/MS to be the dimer of the starting silacyclobutane. Mass spectroscopy showed peaks at: 185 ($M - CH_3$), 157 ($M - CH_3 - Si$, base peak), 129. Rhodium trichloride catalysis under similar conditions gave none of this product, based on GC assay.

4.10. Platinum catalyzed dimerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane

Enough pentane solution of the divinyltetramethyldisiloxane stabilized platinum catalysis was added to a solution of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (0.50 g; 3.5 mmol) to give a platinum/silicon ratio of approximately 1/5000. The mixture was heated under reflux for 30 min. GC monitoring of the mixture revealed the formation of a major product, shown by GC/MS to be a dimer of the starting material. Mass spectroscopy showed peaks at: 273 ($M - CH_3$), 201, 185 and 73 (base peak) among other peaks.

References and notes

1 K. Tamao, T. Tanaka, T. Nakajima, R. Sumiya, H. Arai and Y. Ito, *Tetrahedron Lett.*, *27* (1986) 3377.

2 K. Tamao, T. Nakajima, R. Sumiya, H. Arai, N. Higuchi and Y. Ito, *J. Am. Chem. Soc.*, *108* (1986) 6090.

3 K. Tamao, Y. Nakagawa, H. Arai, N. Higuchi and Y. Ito, *J. Am. Chem. Soc.*, *110* (1988) 3712.

4 K. Tamao, Y. Nakagawa and Y. Ito, *J. Org. Chem.*, *55* (1990) 3438.

5 T. H. Lane and C. L. Frye, *J. Organomet. Chem.*, *172* (1979) 213.

6 A. G. Brook *et al.*, *Organometallics*, *6* (1987) 1246.

7 M. L. Tumey, *Ph.D. Dissertation*, Iowa State University, Ames, IA, 1979.

8 The structure **VIII** possesses two asymmetric centers and therefore should exist in 3 stereoisomeric forms. No attempt was made to characterize the configurational make-up of our product.

9 Thermolysis of 1,5-dioxa-2,6-disilacyclooctaves to yield 1,3-dioxa-2,4-disilacyclohexanes have been reported by Tumey [7] and by Park *et al.* [11].

10 C. Eaborn, *Organosilicon Compounds*, Butterworths, London, 1960, pp. 137–138.

11 Y. T. Park, G. Manuel, R. Bau, D. Zhao and W. P. Weber, *Organometallics*, *10* (1991) 1586.

12 J. F. Harrod and A. J. Chalk, in I. Wender (ed.), *Organic Synthesis of Metal Carbonyls*, Vol. 2, Wiley, New York, 1977, p. 673.

13 J. Y. Corey, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Organo Silicon Compounds*, Part 1, Wiley, New York, 1989, Chap. 1, p. 6.

14 D. R. Weyenberg and L. E. Nelson, *J. Org. Chem.*, *30* (1965) 2618.

15 W. A. Kriner, *J. Polym. Sci.*, *A-1* (1966) 4444.

16 C. S. Cundy, C. Eaborn and M. Lappert, *J. Organomet. Chem.*, *44* (1972) 291.

17 K. Tamao, T. Hayashi and M. Kumada, *J. Organomet. Chem.*, *114* (1976) C19.