Ruthenium-Catalyzed Silylation of Ethylene by Disilanes

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The bis(dihydrogen) ruthenium complex $RuH_2(H_2)_2(PCy_3)_2$ (**1**) and the ethylene complex $RuH(C_2H_4)[P(\eta^3\text{-}C_6H_8)Cy_2](PCy_3)$ (**2**), obtained by addition of ethylene to **1**, catalyze efficiently the silylation of ethylene with $HSiMe_2SiMe_2H$ (**I**) and with the series of disilanes $HSiMe_2(CH_2)_nSiMe_2H$ ($n = 2$, **II**; $n = 3$, **III**; $n = 4$, **IV**). Reaction of **I** with ethylene produces the monosilanes $(CH_2{=}CH)SiMe_2(CH_2CH_3)$ (**I.b**) and $(CH_3CH_2)SiMe_2(CH_2CH_3)$ (**I.c**) resulting from the cleavage of the Si−Si bond and the functionalization of the Si−H bonds. For **II**−**IV**, three processes, hydrosilylation, dehydrogenative silylation, and cyclization, are in competition, leading to the formation of acyclic monofunctionalized intermediates $HSiMe_2(CH_2)_nSiMe_2(CH{=}CH_2)$ (**II.f**−**IV.f**) and $HSiMe_2(CH_2)_nSiMe_2(CH_2CH_3)$ (**II.g**−**IV.g**), acyclic difunctionalized compounds $(CH_2{=}CH)SiMe_2(CH_2)_nSiMe_2(CH{=}CH_2)$ (**II.a**−**IV.a**), $(CH_2{=}CH)SiMe_2(CH_2)_nSiMe_2(CH_2CH_3)$ (**II.b**−**IV.b**), and $(CH_2CH_3)SiMe_2(CH_2)_nSiMe_2(CH_2CH_3)$ (**II.c**−**IV.c**), together with cyclic products $[(SiMe_2)(CH_2)_3(SiMe_2)](CH{=}CH_2)$ (**II.d**−**IV.d**) and $[(SiMe_2)(CH_2)_3(SiMe_2)](CH_2CH_3)$ (**II.e**−**IV.e**). Kinetic studies reveal a consecutive reaction path for the formation of acyclic difunctionalized compounds via the monofunctionalized intermediates. Saturated and unsaturated cyclic products form concurrently to monofunctionalized disilanes. The rates and the selectivity of the reactions are dramatically influenced by the chain length between the two silicon atoms, the fastest conversion and the highest concentration of vinyl products being observed in the case of a long chain. In contrast, formation of cyclic compounds is favored for $n = 2$ or 3. Mechanistic studies show that different complexes are obtained, depending on the order of addition of ethylene and disilane. In the presence of the disilane **II**, **2** converts into a mixture of $RuH_2\{(\eta^2\text{-}HSiMe_2)_2(CH_2)_2\}(PCy_3)_2$ (**3a**) and $RuH_2(SiMe_2(CH_2)_2SiMe_2H)\{P(\eta^3\text{-}C_6H_8)Cy_2\}(PCy_3)$ (**6**). In contrast, in the presence of ethylene, $RuH_2\{(\eta^2\text{-}HSiMe_2)_2(CH_2)_n\}(PCy_3)_2$ ($n = 2$, **3a**; $n = 3$, **3b**), leads to the formation of a new ethylene complex $RuH_2(C_2H_4)_2(PCy_3)_2$ (**4**). Compound **4** is ultimately converted to **2** after total consumption of the liberated disilane. All these complexes are involved in the catalytic processes.

Introduction

Organosilicon compounds have many industrial applications,[1] hydrosilylation remaining the most documented process since its discovery in the late 1940's.[2] Over the past 2 decades, several transformations of silicon compounds have received increasing interest and have provided efficient routes for designing new silicon-based molecules (bis(silylation),[3,4] homo- and heterodehydrocoupling,[5] metathesis of silicon-containing olefins,[6] silylcarbonylation[7]). However, only scattered reports have appeared concerning the activation of bis(hydrosilane). In the first example published in 1982, the $RhCl(PPh_3)_3$-catalyzed double hydrosilylation of nitriles with $(Me_2SiH)_2(C_6H_4)$ leads to *N*,*N*-disilylated amines and enamines in which both Si−H bonds react with nitriles. In contrast, nitriles are not hydrosilylated with mono(hydrosilane) in the same conditions.[8] $RhCl(PPh_3)_3$ is also an active catalyst for the hydrosilylation of alkenes, alkynes, and ketones with chelating bis(hydrosilanes) $(R_2SiH)_2X$.[9] In this case, the selective monofunctionalization of the silane can be obtained. Similarly, in the presence of $RhCl_3$(Pybox) catalysts (pybox

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is a tridentate nitrogen donor ligand) and ketones, only one Si−H group of 1,2-bis(dimethylsilyl)ethane is converted to the corresponding silyl enol ether.[10] Bis(silylation)[3,4] illustrates the peculiar reactivity of bis(hydrosilane) with various unsaturated substrates (acetylenes, olefins, dienes, carbonyl compounds, nitriles, and azirines).[3,11] The double silylation is predominantly catalyzed by group 10 metals[12] and provides a convenient synthetic route to disilacyclic compounds.

Recently, much attention has focused on homo- and heterodehydrogenative coupling of hydrosilanes and new silicon−oligomer and polymers can thus be obtained by dehydropolymerization of bis(hydrosilanes) $H_3Si-X-SiH_3$ or $H_2SiR-X-SiRH_2$.[5,13−16] This method provides an attractive homogeneous route to SiC ceramic precursors.[17] Dehydrogenative silylation of olefins constitutes also a very important dehydrocoupling reaction for the preparation of silicon-based monomers since it produces, directly from olefins and silanes, vinylsilanes which are versatile synthetic intermediates in organic chemistry.[18] This reaction is now well-documented and is catalyzed predominantly by transition metal complexes of the Fe and Co triad groups, although other transition metal complexes (groups 4 and 10) have also shown catalytic activity.[19] However, despite extensive works, the number of examples of selective synthesis of vinylsilanes is still limited.[20,21] In addition, no study concerning dehydrogenative silylation of olefins with bis(hydrosilanes) has been reported, to our knowledge, even though silicon-based divinyl monomers may represent interesting synthetic intermediates for polymerization and polycondensation processes.[22] Dehydrogenative coupling of hydrosilanes with olefins is often accompanied by byproducts among which hydrosilylation species usually dominate. Olefin isomerization,[20a,23] and hydrogenative oligomerization[24] of vinyl-substituted silanes are both competitive reactions. Isomerization occurs in the presence of Fe, Ru, and Rh catalysts, while hydrogenative oligomerization is catalyzed only by various Ni(0) and Ni(II) complexes. Metathesis of vinyl-substituted silicon compounds and their cross-metathesis with olefins, as well as dehydrogenative silylation of olefins with vinylsilanes, may also be encountered in the presence of Ru and Rh catalysts.[19,25] But these reactions remain much less documented.

We have already shown that the bis(dihydrogen) ruthenium complex $RuH_2(H_2)_2(PCy_3)_2$ (**1**)[26] and the ethylene complex $RuH(C_2H_4)[P(\eta^3\text{-}C_6H_8)Cy_2](PCy_3)$ (**2**), obtained by addition of ethylene to **1**, are precursors to very efficient catalysts for the selective synthesis of triethylvinylsilane.[21] With use of a functionalized monosilane such as allyldimethylsilane, the expected dehydrogenative silylation of ethylene is observed in competition with a redistribution reaction at silicon atom, leading to a divinyl compound.[27] We have recently reported the synthesis and the characterization of the first mononuclear bis(silane) complexes $RuH_2(\eta^2\text{-}H-SiR_2)_2X\}(PR'_3)_2$ (**3**) stabilized by two σ Si−H bonds.[28] These compounds represent an arrested stage in a double oxidative addition reaction that leads to disilacyclic complexes, which have been shown to be key intermediates in silylation processes. These results prompted us to study the silylation of ethylene with bis(hydrosilanes) catalyzed by the ruthenium complexes **1** and **2**. We report here our findings concerning these reactions, including the results of catalytic and mechanistic studies. In particular, the influence of the length of the chain between the two Si−H groups on the silylation reaction has been investigated and, the characterization of a new ruthenium bis(ethylene) complex is also reported.

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Scheme 1. Catalytic Silylation of Ethylene by Disilanes

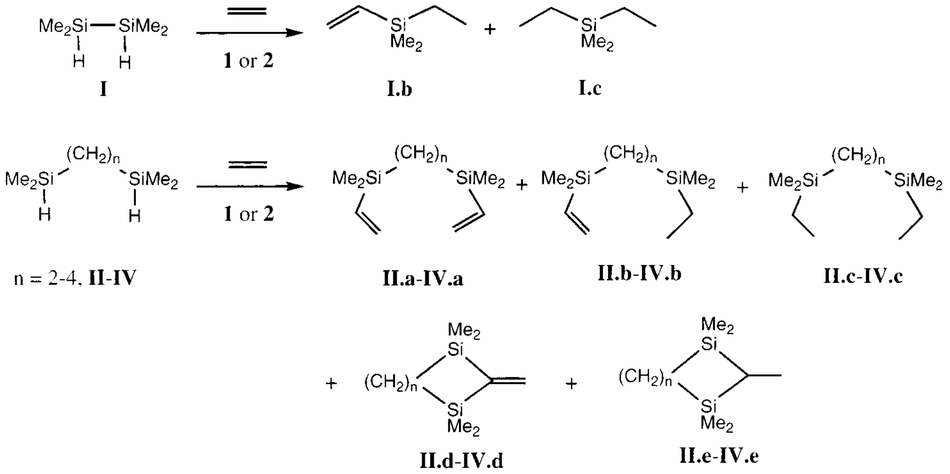

Table 1. Reaction of C_2H_4 with $HSiMe_2SiMe_2H$ (I) Catalyzed by 1 or 2[a]

entry	catalyst	solvent	time (min)	ratio of I.b/I.c (%) I.b	I.c
1	**1**	pentane	350	80	20
2	**2**	pentane	170	78	22
3	**1**	THF	100	90	10
4	**2**	THF	110	79	21

[a] Catalyst/**I** ratio = 1/100; 20 bar of C_2H_4.

Table 2. Reaction of C_2H_4 with $HSiMe_2(CH_2)_2SiMe_2H$ (II) Catalyzed by 1 or 2[a]

entry	catalyst	solvent	time (min)	ratio of II.a/II.e (%) II.a	II.b	II.c	II.d	II.e
1	**1**	pentane	90	16	61	6	4	13
2	**2**	pentane	90	25	29	7	6	33
3	**1**	THF	120	11	62	8	5	14
4	**2**	THF	60	24	34	8	5	29

[a] Catalyst/**II** ratio = 1/100; 20 bar of C_2H_4.

Results

Catalytic Experiments. The study was carried out on $HSiMe_2SiMe_2H$ (**I**) and on a series of disilanes bridged by two to four methylene groups $HSiMe_2(CH_2)_nSiMe_2H$ ($n = 2$, **II**; $n = 3$, **III**; $n = 4$, **IV**) (see Scheme 1). The catalytic experiments were performed at room temperature with ethylene pressure in the range of 5−20 bar in pentane or tetrahydrofuran (THF), and the ruthenium complexes **1** or **2** were used as catalyst precursors. The catalytic activation of **I** differs markedly from the activation of the series **II**−**IV** because it is the only case in which the resulting functionalized product is a monosilicon compound as a result of Si−Si bond cleavage. Within the series of disilanes **II**−**IV**, the reactions adhere to a pattern but the selectivity and activity depend on the chain length of the chosen disilane. Indeed, three processes appear to be in competition and these are illustrated in Scheme 1: (i) hydrosilylation, (ii) dehydrogenative silylation, and (iii) cyclization. In addition the intermediate products $HSiMe_2(CH_2)_nSiMe_2(CH{=}CH_2)$ (**II.f**−**IV.f**) and $HSiMe_2(CH_2)_nSiMe_2(CH_2CH_3)$ (**II.g**−**IV.g**) resulting from the functionalization of only one Si−H bond are observed (see Scheme 2). These intermediates are rapidly consumed, and the functionalization of the second Si−H bond is rapid as inferred from the data obtained in the case of **III**.

$HSiMe_2SiMe_2H$ (I). The reactions were carried out under 20 bar of C_2H_4 at room temperature using a catalyst/disilane ratio of 1/100. The results are summarized in Table 1. Total conversion of the disilane **I** is observed within 2−6 h. The major product using **1** or **2** as catalyst is the mixed compound **I.b** resulting from hydrosilylation of one Si−H bond and dehydrogenative silylation of the second Si−H bond. The best selectivity and rate conversion are obtained in THF.

Thus, in this case, Si−Si bond breaking is very effective since disilane functionalization was not observed. Cleavage of a Si−Si bond has already been reported for stoichiometric additions of disilanes to platinum or cobalt complexes, leading to silyl or silylene structures.[29] For example, formation of the disilyl platinum complex $Pt(SiMe_2H)_2(PEt_3)_2$ is obtained by addition of **I** to $Pt(PEt_3)_3$. This well-established reactivity of Si−Si bonds with transition metals has also been exploited to produce catalytically silylated products.[29d]

$HSiMe_2(CH_2)_2SiMe_2H$ (II). The reactions were carried out under 20 bar of C_2H_4 at room temperature using a catalyst/disilane ratio of 1/100. The results are summarized in Table 2. Total conversion of the disilane **II** is observed within 1−2 h. The major product using **1** as catalyst is the mixed compound **II.b** resulting from hydrosilylation of one Si−H bond and dehydrogenative silylation of the second Si−H bond (see entries 1 and 3). In contrast to this, the use of **2** as catalyst favors the formation of the cyclic product **II.e** and to a lesser extent the divinyl **II.a** (see entries 2 and 4). The nature of the solvent has in these experiments no significant effect. The differences observed in the conversion rates of **II** might result from small variations of the temperature (between 20 and 25 °C).

$HSiMe_2(CH_2)_3SiMe_2H$ (III). In this case, a more detailed study was performed and we have particularly investigated the influence of the catalyst/disilane ratio and of the ethylene pressure. The results are reported in Table 3. Under the same conditions used for the activation of **I** or **II** (entries 1−4), the total consumption of disilane **III** is significantly more rapid than is

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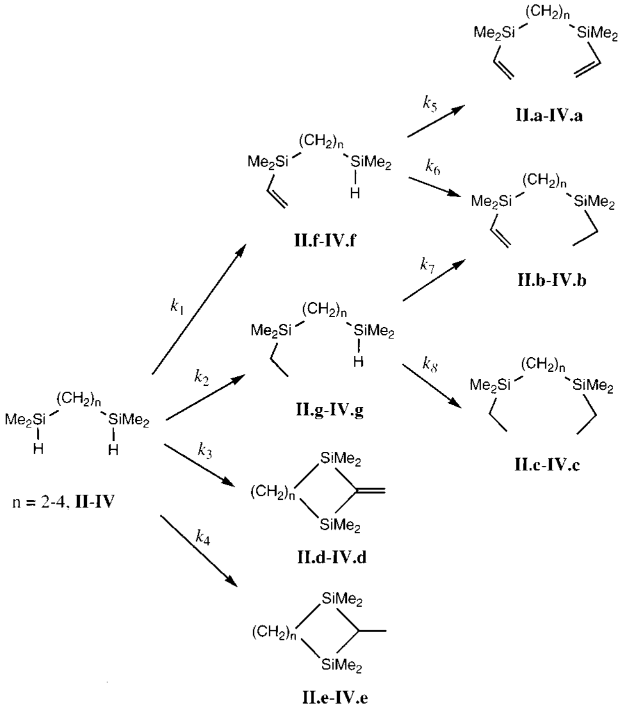
Scheme 2. Concurrent and Consecutive Reactions Involved in the Activation of the Disilanes II−IV Catalyzed by 1 or 2 under Ethylene Pressure



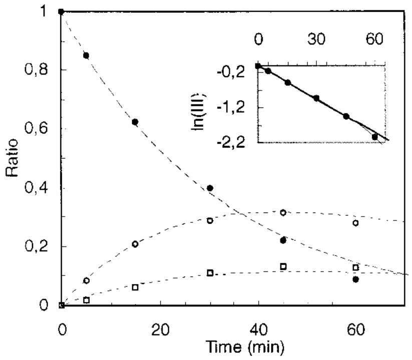


Figure 1. Plot of the disappearance of **III** and formation of **III.f** and **III.g** with time: ●, **III**; ○, **III.f**; □, **III.g**. Inset: Plot of ln(**III**) vs time. The dotted lines exhibit calculated reaction curves (see text).

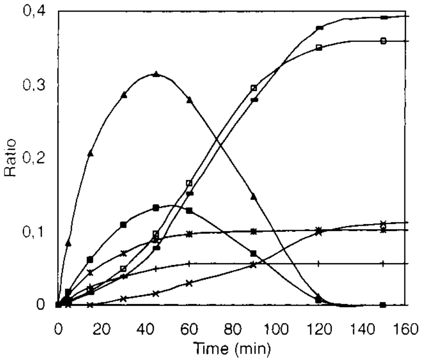


Figure 2. Time dependence of the concentrations of the mono- and difunctionalized products **III.a**−**III.g**: ×, **III.a**; |, **III.b**; □, **III.c**; ∗, **III.d**; +, **III.e**; ▲, **III.f**; ■, **III.g**.

observed for **I** or **II**. Moreover, dehydrogenative silylation is favored, particularly when **1** is employed as the catalyst precursor (entry 3).

The influence of the disilane concentration was studied by varying the catalyst/disilane ratio from 1/50 to 1/500 using **1** as the catalyst source. Inspection of Table 3 reveals that an increase in the disilane concentration induces two effects: (i) total conversion of disilane is achieved after longer reaction times, and (ii) hydrosilylation is favored over dehydrogenative silylation (entries 5, 3, 6, 7). This last observation is confirmed by studying the influence of ethylene pressure from 5 to 20 bar. The reactions were performed with a catalyst (**1**)/disilane (**III**) constant ratio of 1/100: an increase of pressure favors the dehydrogenative silylation process (entries 3, 8−10). Taking optimum conditions, i.e., **1** as catalyst in THF solution under 20 bar of ethylene with a catalyst/disilane ratio of 1/50, leads to an efficient production of **III.a** (58%). Hydrosilylation is disfavored under these conditions as evidenced by our failure to detect **III.c**, and the monovinyl **III.b** is obtained only in 22% yield (entry 5).

$HSiMe_2(CH_2)_4SiMe_2H$ (IV). The selectivity of the reaction is strongly dependent on the nature of the catalyst (see Table 4). Dehydrogenative silylation is highly favored with **1** as catalyst precursor. Compounds **IV.a** and **IV.b** were obtained in 80 and 17% yield, respectively (entry 1). The cyclic compounds are minor products under these conditions. It is also noteworthy that the total conversion is faster than in the previous cases: 7−20 min compared to the 25−120 min required for the total conversion of **II** or **III** under the same experimental conditions.

Kinetic Study of the Catalytic Silylation of Ethylene with III. We have already mentioned the intermediate formation of products resulting from the functionalization of only one Si−H bond $HSiMe_2(CH_2)_nSiMe_2(CH{=}CH_2)$ (**II.f**−**IV.f**) and $HSiMe_2(CH_2)_nSiMe_2(CH_2CH_3)$ (**II.g**−**IV.g**). To gain further insight into the mechanism of the reaction, we have examined in more detail the reaction of **III** with ethylene in the presence of **1**. The reaction was performed under pseudo-first-order conditions by employing a large excess of ethylene (20 bar). The concentrations of the reagent **III,** the products **III.a**−**III.e**, and the intermediates **III.f**, **III.g** were monitored over the course of the reaction by GC. A typical plot of the change in concentration of **III** over time is shown in Figure 1, along with its corresponding ln(**III**) versus time plot. These plots indicate a clean first-order dependence of the reaction rate on the concentration of **III** over 60 min. This time course corresponds to the consumption of more than 85% of the starting material. The rate constant k ($k = k_1 + k_2 + k_3 + k_4$) was found to be $5.3 \times 10^{-4}\ s^{-1}$. Figure 2 shows the variation in the concentration of the products **III.a**−**III.g** as a function of time and clearly reveals consecutive reaction paths (**III** → **III.f** + **III.g**; **III.f** → **III.a** + **III.b**; **III.g** → **III.b** + **III.c**; see Scheme 2). The first step leads to the formation of **III.f** and **III.g** which are converted in a second step into **III.a**−**III.c** as evidenced by the S-shaped curve characteristic of a slow formation at the initial stage. The concentrations of the intermediates **III.f**, **III.g** reach a maximum of 45% after 45 min before total conversion to the difunctionalized products is achieved after 135 min. In contrast, **III.d**−**III.e** are produced concurrently with **III.f** and **III.g**, and their concentration rapidly achieves a limit (less than 10%). The reactions were treated as irreversible pseudo-first-

Table 3. Reaction of C_2H_4 with $HSiMe_2(CH_2)_3SiMe_2H$ (III) Catalyzed by 1 or 2

						ratio of **III.a**/**III.e** (%)				
entry	catalyst	ratio catalyst/**III**	solvent	*P* (bar)	time (min)	**III.a**	**III.b**	**III.c**	**III.d**	**III.e**
1	**1**	1/100	pentane	20	25	33	39	13	9	6
2	**2**	1/100	pentane	20	60	21	46	27	3	3
3	**1**	1/100	THF	20	30	39	31	8	13	9
4	**2**	1/100	THF	20	60	23	48	25	2	2
5	**1**	1/50	THF	20	20	58	22	0	12	8
6	**1**	1/250	THF	20	55	14	39	27	13	7
7	**1**	1/500	THF	20	135	11	39	36	9	5
8	**1**	1/100	THF	5	60	21	43	24	7	5
9	**1**	1/100	THF	10	40	21	43	23	8	5
10	**1**	1/100	THF	15	40	25	40	17	11	7

Table 4. Reaction of C_2H_4 with $HSiMe_2(CH_2)_4SiMe_2H$ (IV) Catalyzed by 1 or 2[a]

				ratio of **IV.a**/**IV.e** (%)				
entry	catalyst	solvent	time (min)	**IV.a**	**IV.b**	**IV.c**	**IV.d**	**IV.e**
1	**1**	pentane	20	80	17	1	2	0
2	**2**	pentane	10	43	39	11	2	5
3	**1**	THF	7	79	16	1	4	0
4	**2**	THF	20	36	45	15	1	3

[a] Catalyst/**IV** ratio = 1/100; 20 bar of C_2H_4.

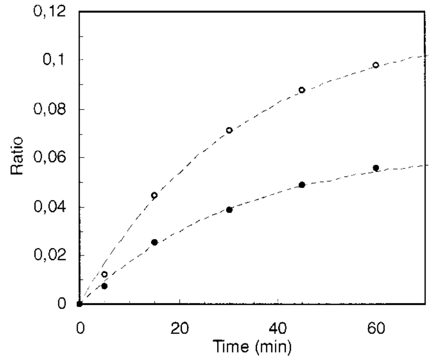


Figure 3. Time dependence of the concentrations of **III.d**, **III.e**: ○, **III.d**; ●, **III.e**. The dotted lines exhibit calculated reaction curves (see text).

order reactions. The rate constants of the reactions leading to **III.d**−**III.g** were obtained by curve fitting to the experimental concentrations ($k_1 = 3.3 \times 10^{-4}$ s^{-1}; $k_2 = 1.1 \times 10^{-4}$ s^{-1}; $k_3 = 6 \times 10^{-5}$ s^{-1}; $k_4 = 3 \times 10^{-5}$ s^{-1}; $k_5 + k_6 = 2.8 \times 10^{-4}$ s^{-1}; $k_7 + k_8 = 1.8 \times 10^{-4}$ s^{-1}; see Figures 1 and 3).[30] However, concentrations of **III.a**−**III.c** (involving k_5−k_8) were found to deviate significantly from the simulated curves. Although a change of reaction order for the second consecutive step appears unlikely, this hypothesis cannot be ruled out. A possible cause could be the concomitance of a concurrent direct path from **III** to **III.a**−**III.c**. On the other hand in such a case, the consecutive reaction path should remain predominant since experimental curves for **III.a**−**III.c** are clearly S-shaped.[31] The complexity of the system prevents us from formulating a more detailed kinetic picture at this time.

Mechanistic Investigations. Characterization of $RuH_2(C_2H_4)_2(PCy_3)_2$. To understand the mechanism of these transformations, several stoichiometric reactions have to be examined. In each case, the reactions of **1** and **2** with C_2H_4 and the disilane have been studied. Compound **2** is obtained by direct reaction of **1** with ethylene. Thus when starting with **1**, two competing reactions take place: (i) reaction with ethylene to generate **2** in situ and (ii) reaction with the disilane to generate the corresponding bis(silane) complex **3** that will further react with ethylene. When using **2** as a starting precursor, the reaction with the disilane should also be examined.

We have already reported the reactivity of **1** with the disilanes **II** and **III** to produce the corresponding bis(silane) complexes $RuH_2\{(\eta^2\text{-}HSiMe_2)_2X\}(PCy_3)_2$ with X = $(CH_2)_2$ (**3a**), $(CH_2)_3$ (**3b**).[28b] It was therefore straightforward to bubble ethylene for 2 min into a C_6D_6 solution of **3b** and monitor the progress of the reaction by ^1H and ^{31}P NMR spectroscopies. After 5 min, ethylene complex **2** was detected as well as a new organometallic species formulated as $RuH_2(C_2H_4)_2(PCy_3)_2$ (**4**). This complex is characterized by a triplet at −11.49 ppm ($J_{P-H} = 31$ Hz) in the ^1H NMR spectrum and a singlet at 62.4 ppm in the $^{31}P\{^1H\}$ NMR which transforms into a triplet upon decoupling only the ^1H of the PCy_3 groups, indicative of the presence of two hydride ligands (see below for additional characterization). A broad signal ($\nu_{1/2} = 44$ Hz) is observed at 5.2 ppm in the ^1H NMR spectrum characteristic of free ethylene participating in a slow exchange process. The bis(silane) ligand was transformed mainly into the divinyl $(CH_2)_3[SiMe_2(CH{=}CH_2)]_2$ **(III.a)** and the cyclic $[(SiMe_2)(CH_2)_3(SiMe_2)](C{=}CH_2)$ **(III.d)** compounds. After 1 h, the ^1H NMR signal attributed to free ethylene is sharp ($\nu_{1/2} = 2$ Hz), and **2** is the only organometallic complex detected. It is worth noting that **4** was also observed when ethylene was added to a complex containing the disiloxane ligand $(HSiR_2)_2X$ (R = Me, Ph; X = O, $OSiMe_2O$). This confirms that, in **4**, no bis(silane) ligand remains coordinated to the ruthenium atom. When ethylene was bubbled for 1.5 min into a C_7D_8 solution of **3b** and the tube was immediately cooled to 243 K, a detailed NMR study was performed at 243 K. This temperature had the advantage of preventing any catalytic reaction and total conversion into **4**, and the free disilane $(HSiMe_2)_2(CH_2)_3$ was observed. One- and two-dimensional ^1H, ^{31}P and ^{13}C NMR measurements at 243 K allow us to propose for **4** the dihydride bis(ethylene) formulation $RuH_2(C_2H_4)_2(PCy_3)_2$. The ethylene ligands coordinated to the

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(30) The calculation was performed with the following rate expressions: $-d[\mathbf{III}]/dt = (k_1 + k_2 + k_3 + k_4)[\mathbf{III}]$; $d[\mathbf{III.d}]/dt = k_3[\mathbf{III}]$; $d[\mathbf{III.e}]/dt = k_4[\mathbf{III}]$; $d[\mathbf{III.f}]/dt = k_1[\mathbf{III}] - (k_5 + k_6)[\mathbf{III.f}]$; $d[\mathbf{III.g}]/dt = k_2[\mathbf{III}] - (k_7 + k_8)[\mathbf{III.g}]$. The amount of each component at time *t* is given as follows: $[\mathbf{III}] = [\mathbf{III}]_0 \exp(-(k_1 + k_2 + k_3 + k_4)t)$; $[\mathbf{III.d}] = k_3/(k_1 + k_2 + k_3 + k_4)[\mathbf{III}]_0(1 - \exp(-(k_1 + k_2 + k_3 + k_4)t)$; $[\mathbf{III.e}] = k_4/(k_1 + k_2 + k_3 + k_4)[\mathbf{III}]_0(1 - \exp(-(k_1 + k_2 + k_3 + k_4)t)$; $[\mathbf{III.f}] = k_1/(k_5 + k_6 - k_1 - k_2 - k_3 - k_4)[\mathbf{III}]_0(\exp(-(k_1 + k_2 + k_3 + k_4)t - \exp(-(k_5 + k_6)t)$; $[\mathbf{III.g}] = k_2/(k_7 + k_8 - k_1 - k_2 - k_3 - k_4)[\mathbf{III}]_0(\exp(-(k_1 + k_2 + k_3 + k_4)t - \exp(-(k_7 + k_8)t)$. These calculations were also confirmed by using the computer simulation program KINSIM: Barshop, B. A.; Wrenn, R. F.; Frieden, C. *Anal. Biochem.* **1983**, *130*, 134.

(31) Hasebe, K.; Kamite, J.; Mori, T.; Katayama, H.; Ozawa, F. *Organometallics* **2000**, *19*, 2030.

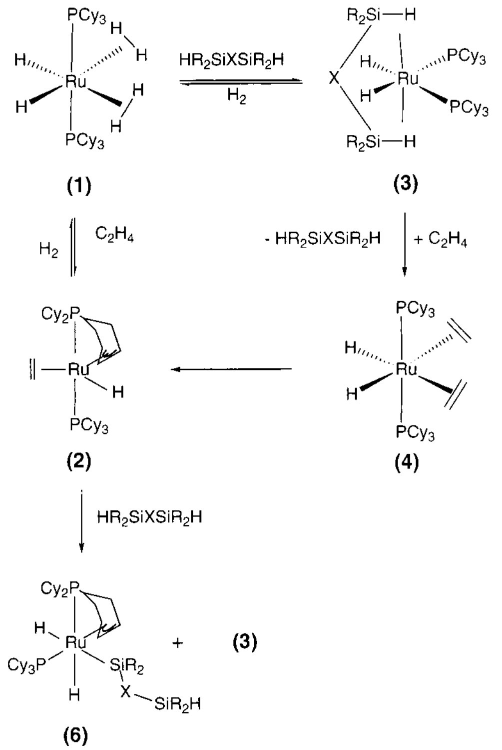
ruthenium atom are characterized by a triplet at 44.7 ppm ($J_{C-H} = 157$ Hz) in the ^{13}C NMR spectrum which correlates with a signal at 2.1 ppm in the ^{1}H NMR spectrum. This area of the spectrum is complicated by the PCy_3 resonances, thus precluding accurate integration to ascertain the presence of two ethylene ligands. Unfortunately, all attempts to isolate **4** from such mixtures resulted in its transformation into **2** accompanied by ethane evolution and the catalytic transformation of disilane into the products of ethylene silylation.

We have already reported the reactivity of **2** with triethylsilane. In this case, the dihydride(silyl) complex $RuH_2(SiEt_3)\{P(\eta^3\text{-}C_6H_8)Cy_2\}(PCy_3)$ (**5**) resulting from oxidative addition of the silane could be isolated and proved to be a catalyst for the dehydrogenative silylation of ethylene.[21] When adding a disilane to **2**, an analogous dihydride(silyl) complex can be characterized together with the formation of the corresponding bis(silane) complex. For example, addition of $HSiMe_2(CH_2)_2SiMe_2H$ (**II**) to a C_6D_6 solution of **2** in a NMR tube leads to a mixture of two compounds: the bis(silane) complex **3a** and the new complex $RuH_2(SiMe_2(CH_2)_2SiMe_2H)\{P(\eta^3\text{-}C_6H_8)Cy_2\}(PCy_3)$ (**6**) resulting from oxidative addition of one Si−H bond. Compound **6** is characterized by ^{1}H and ^{31}P NMR data and by comparison to the previously reported complex **5**. The two hydrides resonate as a broad triplet at −9.41 ppm ($J_{P-H} = 17$ Hz) and a doublet of doublet of doublets at −12.41 ppm ($J_{P-H} = 27$ and 57 Hz, $J_{H-H} = 3.5$ Hz). The allylic moiety is characterized by a pseudo-triplet at 5.01 ppm ($J = 5.6$ Hz) and two broad signals at 2.94 and 3.85 ppm. The free Si−H bond is observed at 4.42 ppm as a septuplet ($J_{H-H} = 3$ Hz). The presence of two inequivalent phosphines is evidenced by the AB spectrum observed in the ^{31}P NMR spectrum at 68.3 and 81.1 ppm with a small J_{P-P} constant of 18.7 Hz indicative of a cis geometry.

Discussion

When considering the **II**−**IV** series, it appears that the reactions go through consecutive steps with the monofunctionalized products as intermediates (see Scheme 2). Under the conditions of 20 bar of ethylene and a constant disilane/catalyst ratio, the percentage of the unsaturated products resulting from dehydrogenative silylation is higher than 45% no matter the nature of the catalyst. The chain length between the two silicon atoms has a dramatic influence on both the rate and the selectivity of the reactions. The fastest conversion and the highest selectivity for vinyl product formation are obtained for the disilane bearing the longest hydrocarbon chain **IV**. As the chain length decreases, the total conversion time increases from 7−20 min for **IV** to 1−2 h for **II**. This may be related to the stability of the bis(silane) complexes obtained by direct reaction of **1** with the corresponding disilane. In particular, calculation of the binding energies showed that the compound derived from **II** is the most thermodynamically stable.[28b] It should be noted that we were not able to isolate a complex derived from **IV**. In the hypothesis of the intermediacy of such compounds in the catalytic cycle, their stability could preclude efficient conversion.

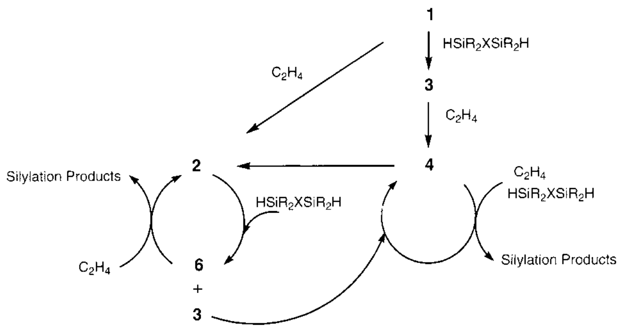
Scheme 3. Stoichiometric Studies



Concerning the selectivity, a comparison with the results obtained previously for monosilane activation[21] indicates a significant difference in mechanism. In the case of monosilanes, we have shown that the formation of vinylsilanes is favored when **2** is used as a precursor. For example, the addition of 1000 equiv of $HSiEt_3$ to **2** at room temperature under 20 bar of ethylene leads to 93% of $CH_2{=}CHSiEt_3$ whereas only 76% are recovered with **1** as catalyst precursor. In contrast, in the case of disilanes, dehydrogenative silylation is higher when using **1** as catalyst (50−91%) versus 46−62% with **2**. Possible explanations for this difference are as follow. (i) Addition of a disilane to **1** results in the formation of a bis(silane) complex **3** which further reacts with ethylene to produce the bis(ethylene) complex **4**. It should be noted that **4** is detected when some disilane still remains in solution (ultimately, **4** will transform into **2** in the absence of disilane) and that it was never observed when using a monosilane. (ii) Compound **1** reacts with ethylene to produce **2**, which can further react with a monosilane or a disilane to produce a complex of ruthenium(IV) resulting from oxidative addition. However in the case of the disilane, formation of the corresponding bis(silane) complex is also observed. The information provided here allows the construction of a complicated system pictured in Scheme 3. The routes differ by the order in which ethylene and the disilane are added to the ruthenium catalyst precursor.

In our system, we have obtained reasonable yields of the exocyclic products **II.d**, **II.e** and **III.d**, **III.e**. The conversion into the cyclic products is also dependent on the nature of the catalyst and on the chain length. As can be seen from Tables 1−4, the five-membered exocyclic compounds **II.d**, **II.e** are favored probably as a result of the intermediacy of a six-membered metallocyclic complex. In the case of **IV**, the proportion of cyclic products dropped to 2−7%. The link between the two silicon atoms seems too long to favor cyclization. Previous studies have provided evidence supporting the

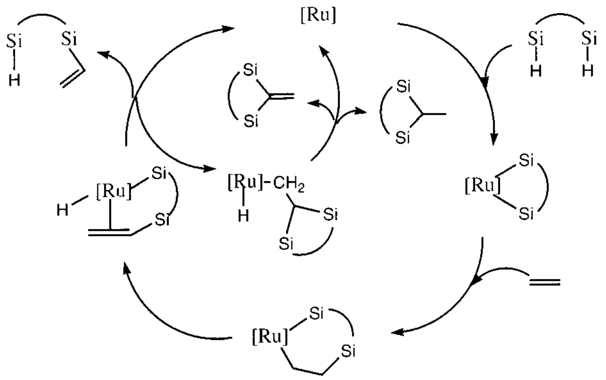
Scheme 4. Catalytic Cycles for the Silylation of Ethylene by Disilanes



intermediacy of bis(silyl)metal species in double silylation.[8-11] Cyclic bis(silyl)metal complexes are easily obtained from the oxidative addition of a disilane to a precursor possessing two accessible vacant coordination sites. Compounds **1** and **3** are complexes stabilized by two σ-H−X bonds (X = H, **1**; X= Si, **3**), and we have previously demonstrated the lability of these ligands. We have shown that $RuH_2(C_2H_4)_2(PCy_3)_2$ (**4**), which has two ethylene ligands that should be easily displaceable, is generated from **1** via **3**. Thus, **4** could be a good candidate to favor the cyclization. This is illustrated by the yields of **III.d** and **III.e** obtained when using **1** as catalyst precursor (15% in pentane and 22% in THF), whereas in the case of **2**, only ca. 5% are recovered. However, the results reported in Table 2 for **II** show that the yield of the cyclic products is substantially higher when using $RuH(C_2H_4)[P(\eta^3\text{-}C_6H_8)Cy_2](PCy_3)$ (**2**) instead of **1** as catalyst precursor. Although addition of **II** (or **III**) to **2** results in the formation of **6** and **3**, and thus generation of **4** is still possible, the concentration of **4** will remain lower than if the catalysis was performed with **1** as starting precursor. The higher concentration of the cyclic products **II.d**, **II.e** (entries 2, 4 versus 1, 3) is thus in contradiction, with **4** being the only species responsible for cyclization. Consequently, **2** must also be involved in another catalytic cycle leading to cyclic products and, presumably in the same time, to other silylated products. These observations suggest that **2** and **4** can serve as precursors to active species involved in different catalytic cycles, as depicted in Scheme 4.

It is interesting that during these experiments endocyclic compounds (i.e., CH_2CH_2 or CH=CH between the two Si atoms) were not observed at any stage, in contrast with previous reports in related systems.[32] For example, whereas hydrosilylation of acetylenic disilanes $HMe_2Si(CH_2)_nSiMe_2C{\equiv}CR$ in the presence of H_2PtCl_6 gave quantitative formation of exocyclic products for $n = 2$, a small increase in the organic chain length ($n = 3$) led to appreciable generation of endocyclic products (21%).[32a] In the presence of the platinum complexes $Pt(CH_2{=}CH_2)(PPh_3)_2$ or $Pt_2(dba)_3$, addition of *o*-bis(dimethylsilyl)benzene to acetylene leads to the exclusive formation of endocyclic products. In contrast, long and flexible chains favor the formation of a large amount of simple acyclic hydrosilylation byproducts. The effect of the structure of the bis(hydrosilane) compounds on the reaction course is presumably associated with the ease of formation of the cyclic bis(silyl)metal species which are key intermediates in these processes.[8-12,33] For example, platinum-catalyzed silylation of 2,2-divinyladamantane illustrates the critical importance of the bis(hydrosilane) geometry.[34] In our system, a possible mechanism for the formation of exocyclic products is shown in Scheme 5. It involves the succession of elementary steps for which unfortunately we have no direct evidence.

Scheme 5. Proposed Mechanism for the Formation of the Exocyclic Products



Detailed mechanisms remain to be clarified and, in particular, the relative involvement of **2** and **4** and the consequences in terms of silylated/hydrosilylated/cyclic products ratio.

Conclusion

This study reveals that catalytic activation of disilanes by the ruthenium complexes **1** or **2** is a more complicated system than the one previously described for the activation of monosilanes.[21] It is remarkable that we always observe difunctionalized products, whereas on the other hand the $RhCl(PPh_3)_3$-catalyzed hydrosilylation of unsaturated molecules results in the activation of only one Si−H bond.[9] In our system, the acyclic difunctionalized silicon products derive from monofunctionalized intermediates, whereas the exocyclic compounds are formed in the early stages of the reaction directly from the disilane. Our results show that the product distributions vary considerably depending on the catalyst precursor and the chain length of the disilane. However, dehydrogenative silylation of disilane is favored over hydrosilylation. The selectivity and activity are highly dependent on the chain length n of the disilane $HSiR_2(CH_2)_nSiR_2H$. In the case of $n = 4$, very high selectivity in divinylsilane was achieved using **1** as catalyst precursor, with almost no formation of cyclic products. It should be noted that all the vinyl products can be converted into hydrosilylated compounds by catalytic hydrogenation using the same catalytic mixture (by replacing ethylene by dihydrogen at the end of the experiments). The stoichiometric studies have allowed us to characterize a new ethylene complex **4**. The detection of **4** is informative, since it

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(32) (a) Steinmetz, M. G.; Udayakumar, B. S. *J. Organomet. Chem.* **1989**, *378*, 1. (b) Swisher, J. V.; Chen, H. H. *J. Organomet. Chem.* **1974**, *69*, 83.

(33) (a) Kang, Y.; Lee, J.; Kong, Y. K.; Kang, S. O.; Ko, J. *Chem. Commun.* **1998**, 2343. (b) Kang, Y.; Kang, S. O.; Ko, J. *Organometallics* **1999**, *18*, 1818. (c) Kang, Y.; Kang, S. O.; Ko, J. *Organometallics* **2000**, *19*, 1216.

(34) Giraud, L.; Jenny, T. *Organometallics* **1998**, *17*, 4267.

could be responsible for the distinct behavior observed for monosilane versus disilane activation. Two catalytic cycles could then compete, although little is known concerning the mechanistic details of these two cycles, as several intervening steps are necessary to explain the generation of the difunctionalized silicon compounds (oxidative addition, insertion, migration, reductive elimination). Furthermore, the role of the $\mathrm{PCy_3}$ ligand should be evaluated. It plays a significant role in the cycle involving **2** and may permit the formation of unsaturated species by successive hydrogen transfer and monodentate or bidentate cooordination via the phosphorus atom and η^2 or η^3 coordination of one cyclohexenyl ring.[35]

Experimental Section

General Considerations. All reactions were carried out under argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled according to standard procedures and degassed prior to use. All reagents were purchased from Aldrich except $\mathrm{RuCl_3 \cdot 3H_2O}$ from Johnson Matthey Ltd. and were used without further purification. The following chemicals were prepared according to published procedures: $\mathrm{RuH_2(H_2)_2(PCy_3)_2}$,[35] $\mathrm{RuH_2[(\eta^2\text{-}HSiMe_2)(CH_2)_2](PCy_3)_2}$,[28] $\mathrm{RuH_2[(\eta^2\text{-}HSiMe_2)(CH_2)_3](PCy_3)_2}$,[28] $\mathrm{RuH(C_2H_4)[(\eta^3\text{-}C_6H_8)PCy_2](PCy_3)}$,[21] $\mathrm{(Me_2SiH)_2}$,[36] $\mathrm{(Me_2SiH)_2(CH_2)_3}$,[37] $\mathrm{(Me_2SiH)_2(CH_2)_4}$.[38] NMR spectra were recorded in $\mathrm{C_6D_6}$ or $\mathrm{C_7D_8}$ on Bruker AC 200 or AMX 400 instruments. GC and GC-MS spectra (EI, 70 eV) were recorded on HP 5890 and HP 5970 MSD spectrometers.

General Procedure for Catalytic Double Silylation of Ethylene with the Bis(hydrosilanes) I–IV. A mixture of the ruthenium catalyst and the bis(hydrosilane) dissolved in a dry solvent was stirred at room temperature for 10 min. The solution was transferred in a 100 mL stainless steel autoclave equipped with a stirring bar. Then, the autoclave was charged with ethylene. The progress of the reaction was monitored by GC, and the bifunctionalized organosilanes were identified by GC-MS analysis, by NMR data, and by comparison with literature data (cyclization products).[32a]

In Situ Monitoring of the Reaction between a Bis(silane) Complex and Ethylene. Characterization of 4. In a typical example, ethylene was bubbled through the $\mathrm{C_6D_6}$ solution of $\mathrm{RuH_2[(\eta^2\text{-}HSiMe_2)(CH_2)_3](PCy_3)_2}$ (20 mg in 0.5 mL of $\mathrm{C_6D_6}$) for 2 min. The tube was maintained at 293 K, and ^{1}H NMR spectra were acquired at regular intervals.

Characterization of **4** was achieved following this procedure: ethylene was bubbled at room temperature through a $\mathrm{C_7D_8}$ solution of $\mathrm{RuH_2[(\eta^2\text{-}HSiMe_2)(CH_2)_3](PCy_3)_2}$ (20 mg in 0.5 mL of $\mathrm{C_7D_8}$) for 1.5 min. The tube was then cooled to 243 K and introduced into the NMR probe at this temperature for measurements.

Compound 4: ^{1}H NMR (400.14 MHz, $\mathrm{C_7D_8}$, 243 K) δ 5.54 (br s, $\mathrm{C_2}H_4$), 1.33–2.44 (m, 66H, $\mathrm{P(C_6}H_{11})_3$), −11.08 (t, $J_{\mathrm{P-H}} = 31$ Hz, 2H, $\mathrm{Ru}H_2$). ^{31}P NMR (161.96 MHz, $\mathrm{C_7D_8}$, 243 K): δ 65.1 (s, $P\mathrm{(C_6H_{11})_3}$). ^{13}C NMR (100.61 MHz, $\mathrm{C_7D_8}$, 243 K): δ 44.7 (t, $^1J_{\mathrm{C-H}} = 157$ Hz, $C_2\mathrm{H_4}$), 39.7 (d, $^1J_{\mathrm{C-H}} = 125$ Hz, $\mathrm{P(C_6H_{11})_3}$), 30.6 (t, $^1J_{\mathrm{C-H}} = 119$ Hz, $\mathrm{P(C_6H_{11})_3}$), 28.4 (t, $^1J_{\mathrm{C-H}} = 120$ Hz, $\mathrm{P(C_6H_{11})_3}$), 26.6 (t, $^1J_{\mathrm{C-H}} = 129$ Hz, $\mathrm{P(C_6H_{11})_3}$).

GC-MS Analysis of the Products. These are given in the following format: *m*/*z* (relative intensity).

Silylation of $\mathrm{HSiMe_2Me_2SiH}$ (**I**). $\mathrm{(CH_2{=}CH)SiMe_2(CH_2CH_3)}$: 114 ($\mathrm{M^+}$, 1), 99 (11), 85 (100), 71 (43), 59 (61) 43 (21). $\mathrm{(CH_3CH_2)SiMe_2(CH_2CH_3)}$: 116 ($\mathrm{M^+}$, 4), 101 (9), 87 (87), 73 (26), 59 (100) 43 (20).

Silylation of $\mathrm{HSiMe_2(CH_2)_2Me_2SiH}$ (**II**). $\mathrm{(CH_2{=}CH)SiMe_2(CH_2)_2Me_2Si(CH{=}CH_2)}$: 198 ($\mathrm{M^+}$, 2), 155 (43), 97 (17), 85 (100), 59 (75). $\mathrm{(CH_3CH_2)SiMe_2(CH_2)_2Me_2Si(CH{=}CH_2)}$: 200 ($\mathrm{M^+}$, 1), 171 (33), 87 (29), 85 (46), 59 (100). $\mathrm{(CH_3CH_2)SiMe_2(CH_2)_2Me_2Si(CH_2CH_3)}$: 202 ($\mathrm{M^+}$, 10), 173 (42), 87 (76), 73 (30), 59 (100). $\mathrm{[Me_2Si(CH_2)_2Me_2Si]C{=}CH_2}$: 170 ($\mathrm{M^+}$, 50), 155 (81), 127 (100), 73 (54), 59 (35). $\mathrm{[Me_2Si(CH_2)_2Me_2Si]CHCH_3}$: 172 ($\mathrm{M^+}$, 54), 157 (85), 129 (100), 97 (38), 73 (20), 59 (36).

Silylation of $\mathrm{HSiMe_2(CH_2)_3Me_2SiH}$ (**III**). $\mathrm{(CH_2{=}CH)SiMe_2(CH_2)_3Me_2Si(CH{=}CH_2)}$: 184 (55), 169 (89), 155 (61), 143 (56), 141 (56), 127 (55), 111 (77), 99 (70), 97 (81), 87 (58), 85 (100), 59 (88). $\mathrm{(CH_3CH_2)SiMe_2(CH_2)_3Me_2Si(CH{=}CH_2)}$: 185 (98), 184 (88), 157 (62), 143 (61), 131 (82), 111 (92), 99 (87), 87 (91), 85 (100), 59 (97). $\mathrm{(CH_3CH_2)SiMe_2(CH_2)_3Me_2Si(CH_2CH_3)}$: 187 (96), 159 (74), 113 (87), 99 (89), 87 (100), 85 (61), 59 (99). $\mathrm{[Me_2Si(CH_2)_3Me_2Si]C{=}CH_2}$: 184 ($\mathrm{M^+}$, 84), 171 (64), 169 (100), 143 (72), 141 (95), 129 (64), 127 (66), 85 (74), 83 (70), 73 (86), 59 (78). $\mathrm{[Me_2Si(CH_2)_3Me_2Si]CHCH_3}$: 186 ($\mathrm{M^+}$, 83), 171 (100), 143 (94), 129 (82), 115 (72), 85 (78), 73 (82), 59 (82).

Silylation of $\mathrm{HSiMe_2(CH_2)_4Me_2SiH}$ (**IV**). $\mathrm{(CH_2{=}CH)SiMe_2(CH_2)_4Me_2Si(CH{=}CH_2)}$: 170 (4), 99 (7), 97 (11), 87 (11), 85 (100), 73 (4), 59 (48), 43 (10). $\mathrm{(CH_3CH_2)SiMe_2(CH_2)_4Me_2Si(CH{=}CH_2)}$: 199 (13), 99 (19), 87 (39), 85 (100), 73 (13), 59 (59).

NMR Data for the Cyclic Products. Compound **III.e.** ^{1}H NMR (300.13 MHz, $\mathrm{CDCl_3}$): δ 1.87 (m, 2H, $\mathrm{C}H_2\mathrm{-CH_2-Si}$), 1.02 (d, $^3J_{\mathrm{H-H}} = 7.4$ Hz, 3H, $\mathrm{CH-C}H_3$), 0.66 (m, 4H, $\mathrm{C}H_2\mathrm{-Si}$), 0.093 (s, 6H, $\mathrm{Si(C}H_3)_2$), 0.085 (s, 6H, $\mathrm{Si(C}H_3)_2$), −0.19 (q, $^3J_{\mathrm{H-H}} =$ 7.4 Hz, 1H, $\mathrm{C}H\mathrm{-CH_3}$). ^{13}C NMR (75.47 MHz, $\mathrm{CDCl_3}$): δ 8.5 (qd, $^1J_{\mathrm{C-H}} = 126.6$ Hz, $^2J_{\mathrm{C-H}} = 4.8$ Hz, $\mathrm{CH-}C\mathrm{H_3}$), 6.3 (d, $^1J_{\mathrm{C-H}} = 107.0$ Hz, $C\mathrm{H-CH_3}$), 19.1 (t, $^1J_{\mathrm{C-H}} = 126.1$ Hz, $C\mathrm{H_2-CH_2-Si}$) or 18.2 (t, $^1J_{\mathrm{C-H}} = 115.5$ Hz, $C\mathrm{H_2-CH_2-Si}$), 17.2 (t, $^1J_{\mathrm{C-H}} =$ 116.0 Hz, $C\mathrm{H_2-Si}$), 1.4 (q, $^1J_{\mathrm{C-H}} = 118.0$ Hz, $\mathrm{Si(}C\mathrm{H_3)_2}$), −1.6 (q, $^1J_{\mathrm{C-H}} = 118.7$ Hz, $\mathrm{Si(}C\mathrm{H_3)_2}$).

Compound **III.d**. ^{1}H NMR (300.13 MHz, $\mathrm{CDCl_3}$): δ 6.23 (s, 2H, $\mathrm{C{=}C}H_2$), 1.93 (m, 2H, $\mathrm{C}H_2\mathrm{-CH_2-Si}$), 0.71 (m, 4H, $\mathrm{C}H_2\mathrm{-Si}$), 0.00 (s, 6H, $\mathrm{Si(C}H_3)_2$), −0.01 (s, 6H, $\mathrm{Si(C}H_3)_2$). ^{13}C NMR (75.47 MHz, $\mathrm{CDCl_3}$): δ 154.1 (s, $C\mathrm{{=}CH_2}$), 137.5 (t, $^1J_{\mathrm{C-H}} = 155$ Hz, $\mathrm{C{=}}C\mathrm{H_2}$), 18.2 (t, $^1J_{\mathrm{C-H}} = 115.5$ Hz, $C\mathrm{H_2-CH_2-Si}$) or 19.1 (t, $^1J_{\mathrm{C-H}} = 126.1$ Hz, $C\mathrm{H_2-CH_2-Si}$), 17.2 (t, $^1J_{\mathrm{C-H}} = 116.0$ Hz, $C\mathrm{H_2-Si}$), −2.4 (q, $^1J_{\mathrm{C-H}} = 119.0$ Hz, $\mathrm{Si(}C\mathrm{H_3)_2}$), −4.2 (q, $^1J_{\mathrm{C-H}} = 118.3$ Hz, $\mathrm{Si(}C\mathrm{H_3)_2}$).

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