On the possible formation of Si=O, Si=S, and Si=Se double bonds via the reaction of silylenes with oxirane, thiirane, and selenirane, respectively. An ab initio theoretical study

Yitzhak Apeloig and Stepan Sklenak

Abstract: The reactions between silylene, H_2Si, and the three-membered ring compounds, oxirane (**9**), thiirane (**10**), and selenirane (**11**), which provide possible routes to Si=X (X = O, S, Se) double bonds were studied by ab initio calculations at the MP2 and QCISD correlated levels of theory employing the polarized 6-31G** basis set. The calculations show that the three reactions are all *highly exothermic*, (–61.8, –45.2, –52.9 kcal/mol at MP2/6-31G**//MP2/6-31G** for X = O, S, Se, respectively). In the gas phase, at 0 K, these reactions are predicted to be also spontaneous (i.e., the calculated transition states are lower in energy than the reactants). At 298 K, entropy contributions result in small barriers on the ΔG surface for X = O, S (7.4 kcal/mol for both reactions at QCISD (full)/6-31G**), but for X = Se the reaction remains spontaneous. Thus, the calculations suggest that these reactions are viable routes for the preparation of compounds with Si=X (X = O, S, Se) double bonds. The first step in all the reactions is the barrier-less formation of an encounter-complex between the silylene and the X atom of the precursor. For X = O, S, these complexes are predicted to be sufficiently stable to be observed in a matrix. The reaction steps which follow depend on X; for X = O fragmentation of the silylene–XC_2H_4 complex proceeds in two steps via a *biradical* intermediate, while for X = S and X = Se the fragmentation occurs in *a single step*. The first ab initio calculations for H_2Si=Se are reported.

Key words: silylene, silanone, silanethione, silaneselone.

Résumé : Faisant appel à des calculs ab initio aux niveaux MP2 et QCISD apparentés de la théorie et utilisant l'ensemble polarisé 6-31G**, on a étudié les réactions entre le silylène, H_2Si, et les composés cycliques à trois chaînons oxirane (**9**), thiirane (**10**) et sélénirane (**11**) qui pourraient servir de voies à la formation de doubles liaisons Si=X (X = O, S, Se). Les calculs montrent que les trois réactions sont toutes *très exothermiques* (–61,8, –45,2 et –52,9 kcal/mol au niveau MP2/6-31G**//MP2/6-31G** pour X = O, S et Se respectivement). En phase gazeuse, à 0 K, il est aussi prédit que ces réactions seront spontanées (c'est-à-dire que l'énergie des états de transitions est plus faible que l'énergie des réactifs). À 298 K, les contributions de l'entropie conduisent à de faibles barrières sur la surface du ΔG pour X = O et S (7,4 kcal/mol pour chacune des réactions au niveau QCISD(plein)/6-31G**)); toutefois, pour X = Se, la réaction reste spontanée. Ainsi les calculs suggèrent que ces réactions sont viables pour la préparation de composés comportant une double liaison Si=X (X = O, S, Se). La première étape de toutes ces réactions est une formation sans barrière d'énergie d'un complexe de rencontre entre le silylène et l'atome X du précurseur. Pour X = O et S, il est prédit que ces complexes sont suffisamment stables pour être observés dans une matrice. Les étapes réactionnelles qui suivent dépendent de la nature de X; pour X = O, la fragmentation du complexe silylène–XC_2H_4 se produit en deux étapes par le biais d'un intermédiaire *biradical* alors que pour X = S et X = Se, la fragmentation se produit en *une seule étape*. On rapporte aussi les premiers calculs ab initio pour le H_2Si=Se.

Mots clés: silylène, silanone, silathione, silanesélone.

[Traduit par la Rédaction]

Introduction

The synthesis of compounds with multiple bonds to silicon is one of the important contemporary challenges in silicon chemistry (1). For many years such compounds were known only as transients and stable compounds with multiple bonds to silicon were isolated only in the last two decades (1). Of the R_2Si=X (X = O, S, Se) family, a stable

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Dedicated to Professor Adrian G. Brook, one of the great pioneers of modern organosilicon chemistry.

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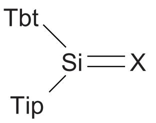
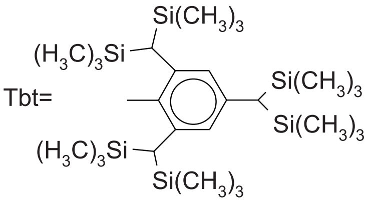
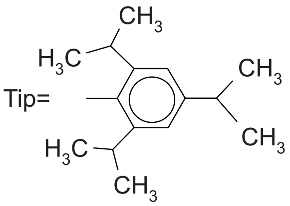
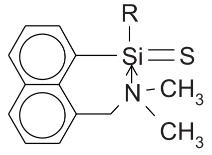


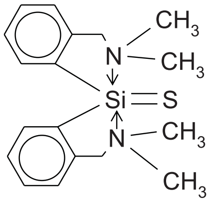
1 (X=S)
2 (X=Se)







3a (R = phenyl)
3b (R = 1 - naphthyl)



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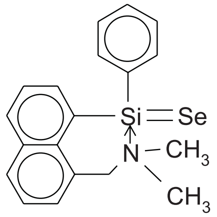

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silanethione $R_2Si{=}S$ (**1**) (2) and a stable silaneselone $R_2Si{=}Se$ (**2**), (3) which are kinetically stabilized by the very bulky substituents Dip (2,6-$^i Pr_2C_6H_3$), Tip (2,4,6-$^i Pr_3C_6H_2$), and Tbt (2,4,6–[$(Me_3Si)_2CH$]C_6H_2) were recently isolated by Okazaki and co-workers (2, 3) in two spectacular achievements. All other known silanethiones or silaneselones with a tricoordinated silicon atom are transient species (1, 4, 5). Si=X double bonds can also be stabilized by substituents which can coordinate intramolecularly to the low-coordinated silicon atom. Three such "internally coordinated silanethiones," **3a**, **3b**, and **4**, were recently isolated (6); **3** and **4** have tetracoordinate (6*a*) and pentacoordinate (6*b*) silicon atoms, respectively. An internally coordinated silaneselone (**5**), with a tetracoordinated silicon atom, was also isolated (6*a*). Stable silanones, $R_2Si{=}O$, are not yet known (not even as internally coordinated species as in **3**–**5**), but several transient silanones, including the parent $H_2Si{=}O$ (**6**), (7*a*, *b*) were detected spectroscopically in matrix (7) and in the gas phase (8). The parent silanone $H_2Si{=}O$ (**6**) (1*b*, (for a related theoretical study see ref. 8*c* and 8*e*), 9) and silanethione $H_2Si{=}S$ (**7**) (9*c*, 10) were studied theoretically. In contrast, nothing is currently known, either theoretically or experimentally, on silaneselone $H_2Si{=}Se$ (**8**).

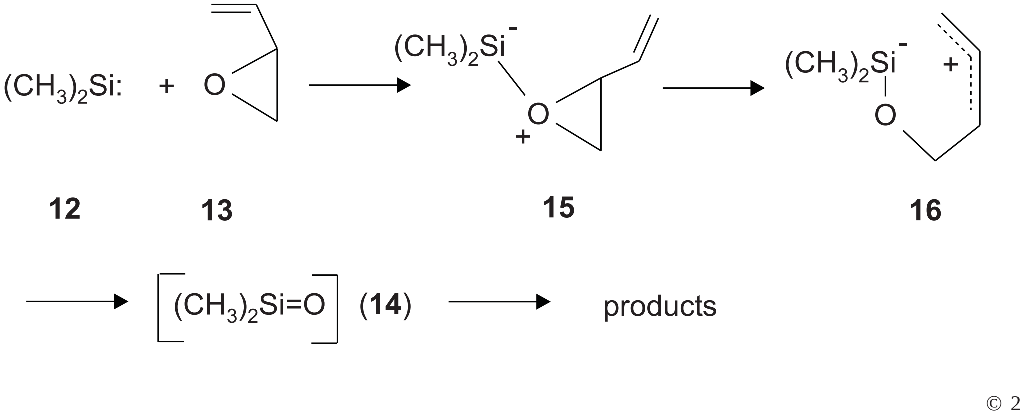
A possible route leading to compounds with a Si=X (X = O, S, Se) double bond is the reaction between a silylene, R_2Si:, and a strained chalcagenide three-membered ring compound, c-C_2H_4X, such as oxirane (X = O, **9**), thiirane (X = S, **10**), or selenirane (X = Se, **11**), as shown in eq. [1].

[1] 

Several experimental studies of the reaction of silylenes with oxiranes have been reported (11). Tzeng and Weber (11*a*) studied the reaction between dimethylsilylene (**12**) and 2-vinyl oxirane (**13**) and based on the observed products they suggested that dimethylsilanone (**14**) is formed as an intermediate (Scheme 1). The proposed mechanism (Scheme 1) involves the initial formation of a silylene–oxirane ylide intermediate **15**, which opens to an allylic ion-pair (**16**), which dissociates to give $(CH_3)_2Si{=}O$. Although the observed products are consistent with the intermediacy of $(CH_3)_2Si{=}O$, the desired dimethylsilanone (**14**) was not directly observed.

Barton (11*b*) and Goure and Barton (11*c*) studied the reaction of $(CH_3)_2Si$ with cyclooctene oxide (**17**). They concluded (Scheme 2) that the ylide **18** is formed, but they could not establish unequivocally if **18** extrudes $(CH_3)_2Si{=}O$, or whether it acts as a "silanone transfer agent" yielding products which are consistent with the presence of **14**. They also could not differentiate between paths A and B in Scheme 2.

Scheme 1.



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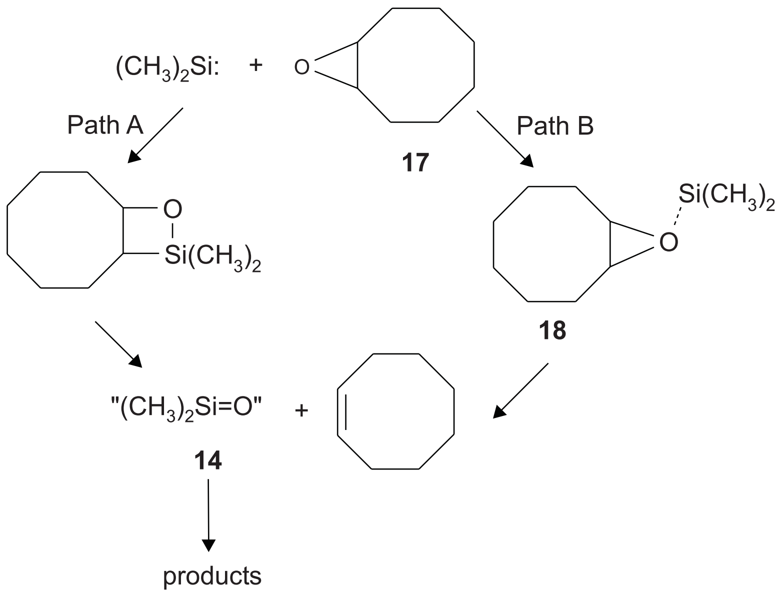
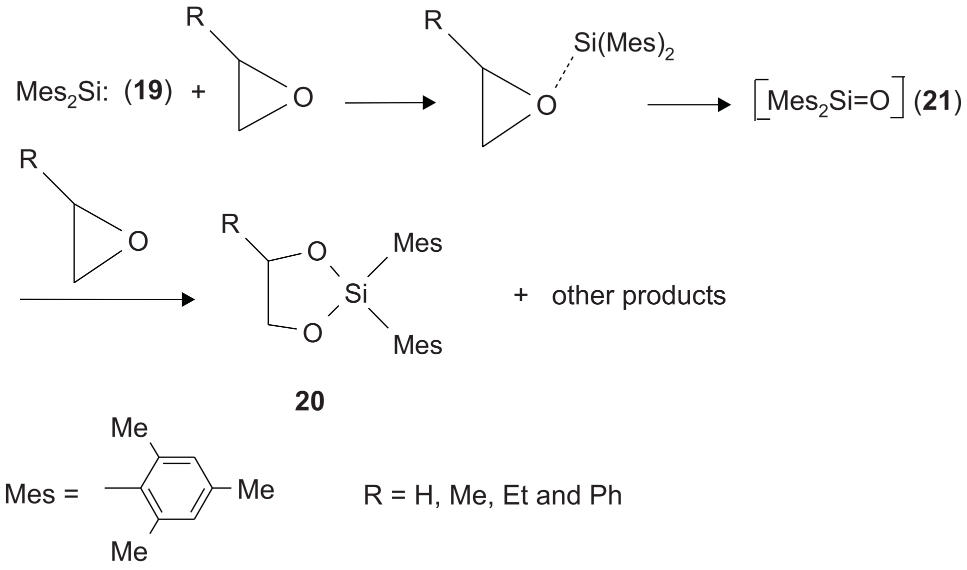
Scheme 2.



Scheme 3.

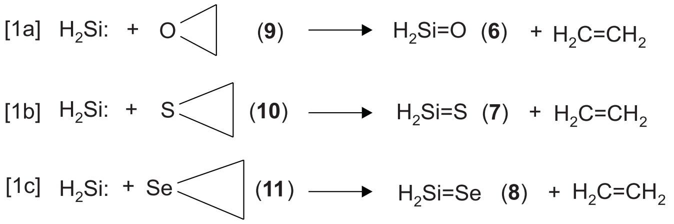


Ando et al. (11*d*), suggested the intermediacy of dimesitylsilanone ($Mes_2Si{=}O$, Mes = 2,4,6-$Me_3C_6H_2$) (**21**) in the reaction of Mes_2Si (**19**) with oxiranes and with several 2-substituted oxiranes (Scheme 3).

In a recent study, Walsh and co-workers (11*e*) studied the gas phase reactions of $(CH_3)_2Si$ with oxirane and interpreted their results in terms of the transient formation of $(CH_3)_2Si{=}O$.

Although a variety of thiiranes, are known (12*a*), only one example of rxn. [1], X = S, between a disilyloxy silylene, $(Me_3SiO)_2Si$ (generated in situ on a reactive silica surface) and a thiirane, was reported, and the intermediacy of a silanethione was suggested (12*b*). There are no reports on the reaction of silylenes with seleniranes; which is not surprising, as the number of available seleniranes is limited. Only one stable tetra-substituted selenirane (13*a*, 13*b*) and two relatively unstable tri-substituted seleniranes (13*c*) are known.

To shed further light on the mechanism of the reactions of silylenes with chalcogenide-3-membered ring compounds and to test whether these reactions are potentially useful for generating Si=X double bonds we have studied rxn. [1] by high-level ab initio molecular orbital calculations. We have attempted to answer questions such as: "Is rxn. [1] exothermic, despite the formation of the high energy $H_2Si{=}X$? Do large energy barriers separate the reactants from the desired products? Are there lower energy channels leading to other products?." Three major model reactions were studied: i.e., the reactions between H_2Si and oxirane (**9**), thiirane (**10**), and selenirane (**11**), potentially leading to $H_2Si{=}X$, X = O, S, Se, respectively, (eqs. [1*a*]–[1*c*]), as well as the reactions of the larger Me_2Si and Mes_2Si (Mes = 2,4,6-$Me_3C_6H_2$-) with oxirane. The computational results and our conclusions about the mechanisms of these reactions are reported in this paper.



Computational methods

Ab initio molecular orbital calculations (14) at the correlated Møller–Plesset MP2 (15) and QCISD (16) levels of theory were performed, using the Gaussian 94 series of programs (17). The fully polarized 6-31G** basis set (18) was used throughout and all electrons were included in the calculations (including for Se). Equilibrium geometries and transition structures were fully optimized at both the MP2(full)/6-31G** and the QCISD(full)/6-31G** (except for H_2Si=Se) levels of theory. Vibrational frequencies at the MP2/6-31G** level were computed for all species, to characterize them as minima, transition structures, or higher order saddle points on the potential energy surface (PES) and for evaluating their zero-point vibrational energies (ZPE). IRC calculations (19) were applied to all the MP2/6-31G** calculated transition structures to secure that they indeed connect the reactants with the desired products.

Enthalpies at 0 K (H_0°) were calculated as the sum of the total energies (either at MP2 or at QCISD) and the corresponding ZPEs calculated at MP2/6-31G**. Entropies (S_{298}°), Gibbs free energies (G_{298}°), and ZPEs at 298 K, were calculated using the ideal gas approximation, as implemented in Gaussian 94 (17). S_{298}° and thus G_{298}° could be calculated directly at the MP2 level. At the QCISD level (where the vibration energies were not calculated) $G°_{298}$ was estimated using the S_{298}° values calculated at MP2/6-31G**.

To simplify the presentation the following designations are used throughout the paper: (*i*) $S°$ and $G°$ (without a subscript) denote these values at 298 K (i.e., $S° = S_{298}^\circ$ and $G° = G_{298}^\circ$, respectively), while $\Delta H°$ denotes this value at 0 K; (*ii*) MP2 and QCISD denote such calculations with the 6-31G** basis set using the optimized geometries at the same levels, i.e., MP2 and QCISD denote MP2/6-31G**/ /MP2/6-31G** and QCISD/6-31G**//QCISD/6-31G** calculations, respectively.

Results

The calculated total energies, ZPEs, entropies, and Gibbs free energies of all species involved in eqs. [1*a*]–[1*c*] are listed in Table 1. Selected geometrical parameters of the optimized structures of the reactants and products are shown in Fig. 1, those of the intermediates and the transition states are given in Table 2 and the atom numbering used is shown in Scheme 4. The calculated enthalpies and Gibbs free energies of eqs. [2*a*]–[2*c*] are given in Table 3. The supplementary material includes the calculated vibration frequencies of the $H_2S\cdots XC_2H_4$ complexes.

The effect of the level of theory which was used on the calculated reaction energies is small for X = S, but somewhat more significant for X = O, where the MP2/6-31G** calculations overestimate $\Delta H°$ of rxn. [1*a*] by 5 kcal/mol (the difference is even higher for the individual reaction steps) relative to QCISD/6-31G**. In general the QCISD/6-31G** values are believed to be the more reliable and therefore QCISD values are generally used in the discussion (unless stated otherwise). The very small difference between the MP2 and QCISD results for eq. [1*b*] (X = S) suggest that this is the case also for eq. [1*c*] (X = Se), where QCISD calculations are beyond our current capabilities.

Discussion

The calculations reported in this paper apply directly to the isolated molecules in the gas-phase and we wish first to point out some of the consequences of this fact. In connection to the bimolecular reactions discussed in this paper, two types of potential energy surfaces (PES), shown in Fig. 2, should be considered: (*i*) an exothermic multistep reaction in which the energy of the reactants is higher than the energy of all the transition states involved (Fig. 2*a*). Such a reaction is spontaneous at 0 K and is expected to occur extremely rapidly. The encounter-complex is produced in a vibrationally excited state having sufficient internal energy to overcome the activation barrier, $\Delta E(1)$, and to proceed to yield the products; (*ii*) an exothermic multistep reaction in which one of the transition states is higher in energy than the energy of the reactants (Fig. 2*b*). In this case the reaction is not spontaneous and the encounter-complex (or other intermediates) will have a significant life time (depending on the height of the $\Delta E(3)$ barrier), because on average the vibrationnally excited molecules do not have the required energy to cross the $\Delta E(3)$ barrier. An additional energy of at least $\Delta E(3)$ has to be supplied to allow the reaction to proceed to the products.

The situation is different in solution (or in high-pressure gas-phase reactions) because the energy gained in the formation of the first encounter-complex (or intermediate) can be rapidly distributed to the environment and the complex can reach its vibrational ground state. So even in case (*i*) (Fig. 2*a*) the encounter-complex will have a significant lifetime and an additional energy of $\Delta E(1)$ has to be supplied to the system to overcome the barrier separating the first encounter-complex from the products. In case (*ii*) (Fig. 2*b*), the energy required in solution to overcome the activation barrier of $\Delta E(2)$ is higher than for the isolated molecules in the gas-phase ($\Delta E(3)$).

The discussion below applies generally to the gas-phase reactions to which the calculations are directly applicable, but in some cases the conclusions are extended to the liquid phase based on the guidelines discussed above.

1. Energetics and mechanism of the reactions of silylene with chalcogenide three-membered rings

Reactions [2*a*]–[2*c*] are calculated to be highly exothermic, both on the enthalpy and on the free energy surfaces (Table 3) i.e., by (ΔG_{298}° values at MP2, kcal/mol): –61.8 for

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Table 1. Calculated absolute energies (Hartrees), zero point energies (ZPE, kcal/mol), entropies (cal mol^{-1} K^{-1}), and Gibbs free energies (Hartrees).

Molecule (level)	MP2/6–31G**[a]	QCISD/6–31G**[b]	ZPE[c]	S°_{298}[c]	G°_{298}[c]
Silanone (**6**)	–365.213082	–365.226555	12.06	56.09	–365.216484
Silanethione (**7**)	–687.821243	–687.848974	11.18	58.94	–687.827266
Silaneselone (**8**)	–2687.911768		10.82	61.85	–2687.919636
Oxirane (**9**)	–153.348235[d]	–153.373619	37.16[e]	57.86	–153.312440
Thiirane (**10**)	–475.982236	–476.015201	35.90	60.63	–475.949604
Selenirane (**11**)	–2476.059698		35.06	63.82	–2476.029732
Dimethylsilylene (**12**)	–368.499000		46.32		
Dimethylsilanone (**14**)	–443.626979		49.63		
O-zwitterion (**22**)	–443.479700	–443.524871	48.48	72.37	–443.430556
S-zwitterion (**23**)	–766.113835	–766.165433	46.65	76.84	–766.069175
Se-zwitterion (**24**)	–2766.207981		45.79	79.66	–2766.165775
O-biradial complex (**25**)	–443.480586	–443.510428	47.29	75.10	–443.434037
O-transition state (**26**)	–443.445958	–443.498331	46.62	71.91	–443.399624
O-transition state (**27**)	–443.474872	–443.505329	45.98	74.07	–443.430206
S-transition state (**28**)	–766.086683	–766.138443	45.10	78.72	–766.045223
Se-transition state (**29**)	–2766.194380		44.71	79.32	–2766.153826
Silaoxetane (**30a**)	–443.597940		49.63		
Silathietane (**30b**)	–766.202552		48.15		
Silaselenetane (**30c**)	–2766.292564		47.47		
Silaoxetane TS (**31a**)	–443.528756		47.57		
Silathietane TS (**31b**)	–766.134320		46.57		
Silaselenetane TS (**31c**)	–2766.229162		46.11		
Dimethylsilanethione (**32**)	–766.233346		48.82		
Dimethylsilaneselone (**33**)	–2766.328298		48.65		
Diphenylsilylene (**34**)	–749.137953[f]		121.75[f]		
Diphenylsilanone (**35**)	–824.064648[f]		124.96[f]		
H_2Si	–290.093976	–290.118691	7.76	49.48	–290.101309
$H_2C{=}CH_2$	–78.327231[g]	–78.355922	32.89[h]	52.29	–78.295689

[a] Using MP2/6–31G** optimized geometries.

[b] Using QCISD/6–31G** optimized geometries.

[c] At MP2/6–31G**.

[d] –152.874064 at HF/6–31G**.

[e] 38.86 kcal/mol at HF/6–31G**.

[f] At HF/6–31G**.

[g] –78.038841 at HF/6–31G**.

[h] 34.20 kcal/mol at HF/6–31G**.

oxirane (eq. [1*a*]), –45.2 for thiirane (eq. [1*b*]) and –52.9 for selenorane (eq. [1*c*]). The calculated reaction enthalpies, Δ*H*°, are very similar to the Δ*G*° values (Table 3). The energies of eqs. [1*a*]–[1*c*] are significantly lower than those calculated for the analogous reactions of singlet methylene, CH_2, (Δ*H*° values at MP2, kcal/mol) with oxirane (–110.0), thiirane (–85.8), and selenorane (–80.0). However, although these reactions are highly exothermic, rxns. [1*a*] and [1*b*] are calculated not to occur spontaneously at 298 K even in the gas-phase because significant barriers (Δ*G* surface) of 7.4 and 7.3 kcal/mol, respectively, separate the reactants from the products. This result has, of course, important experimental consequences which will be discussed below. Only rxn. [1*c*], for X =Se is predicted to occur spontaneously in the gas-phase.

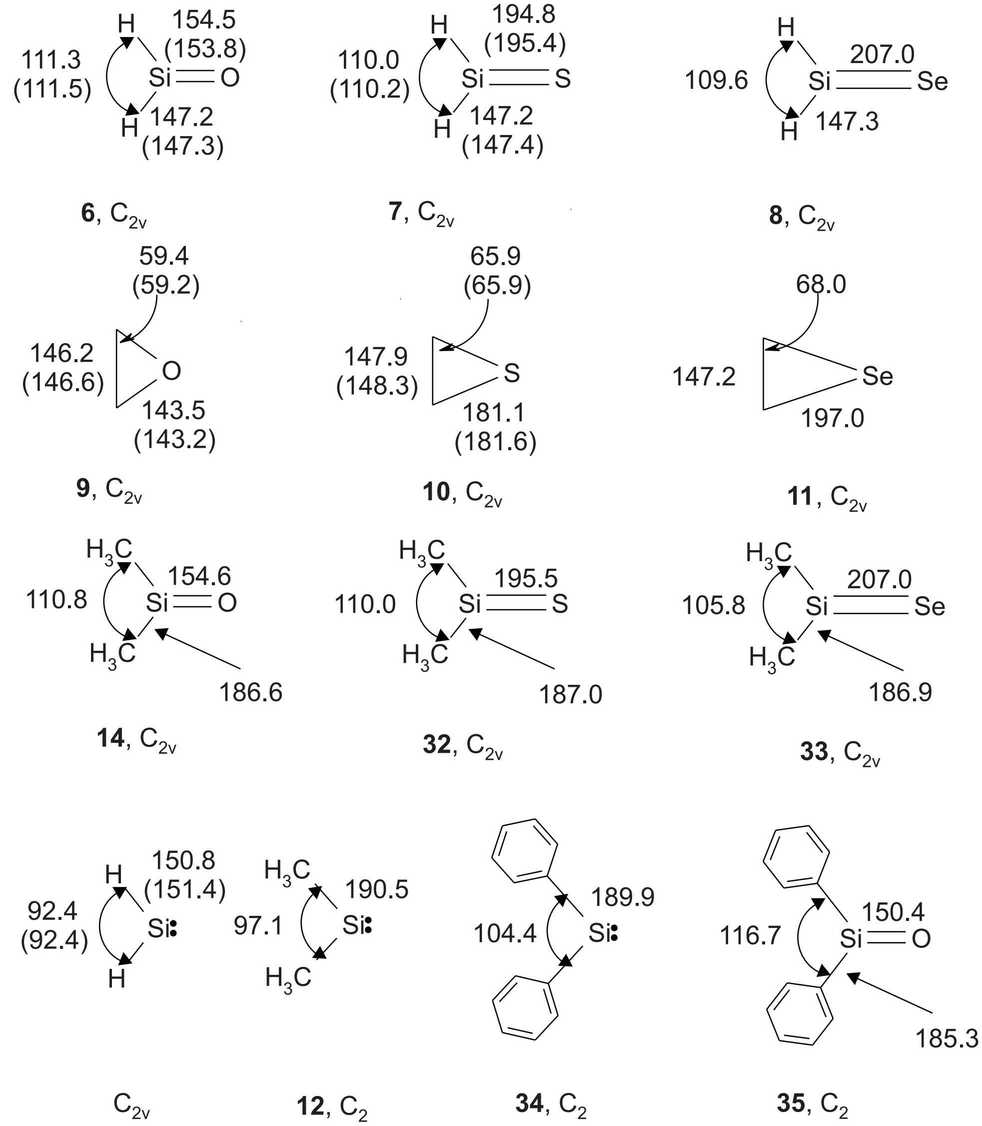
The first step in all three reactions is the attack of H_2Si on the heteroatom X of the three-membered ring to give the corresponding encounter-complex intermediates: (*i*) **22** (X = O, eq. [2*a*]); (*ii*) **23** (X = S, eq. [2*b*]); and (*iii*) **24** ((X = Se, eq. [2*c*]). This step is exothermic and does not involve an energy barrier and it occurs spontaneously both on the enthapy and on the free energy surfaces. However, due to the contribution of entropy this step is much less exothermic (by ca. 9–10 kcal/mol at 298 K) on the ΔG_{298} surface than on the ΔH_{298} surface. The geometries (Table 2) and the electronic nature of the intermediate silylene–XC_2H_4 complexes **22**–**24** are discussed below.

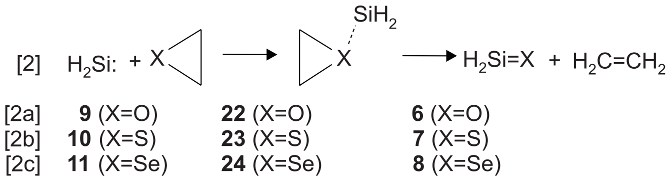
The subsequent reaction steps, leading from the encounter-complex intermediates to the final $H_2Si{=}X + CH_2{=}CH_2$ products, are different for the silylene reaction with oxirane (eq. [2*a*]) and for the reactions with thiirane and selenirane (eq. [2*b*] and eq. [2*c*], respectively), and these reactions are therefore discussed separately.

1. *(a) The reaction of silylene with oxirane*

The calculated enthalpies and Gibbs free energies (at 298 K) for the reaction between H_2Si and oxirane (rxn. [2*a*]) are shown in Figs. 3*a* and 3*b*, respectively. These figures and the

Fig. 1. Selected optimized geometrical parameters at MP2/6–31G** and QCISD/6–31G** (values in parenthesis) of species of interest. Species **34** and **35** are at HF/6-31G**. Bond lengths are given in pm, bond angles in degrees.





discussion below are based on the QCISD/6-31G** values, which are believed to be the more reliable (the MP2/6-31G** values are given in parenthesis). As pointed out above, rxn. [2*a*], although it is very exothermic, $\Delta G°$ = –56.6 kcal/mol (at QCISD/6-31G**) is predicted not to occur spontaneously at 298 K even in the gas-phase, as it involves a significant barrier (i.e., the PES is of type (*b*) in Fig. 2) on the ΔG surface (Fig. 3*b*). On the other hand at 0 K, where the contribution of entropy is zero (Fig. 3*a*), the reaction is spontaneous (i.e., the PES is of type (*a*) in Fig. 2).

In the first step of the reaction, a donor–acceptor complex between H_2Si and oxirane (**22**), which is kinetically stable, is formed. This step is spontaneous and quite exothermic ($\Delta H°$ = –17 – –20, $\Delta G°$ = –7 – –11 kcal/mol), pointing to a stable complex, which should be detectable spectroscopically at low temperatures. Similar complexes between silylenes and ethers or alcohols have been reported and also characterized spectroscopically (20). The calculated vibrational frequencies of the complexes **22**–**24** are reported in the supplementary material to assist in their future spectroscopic identification. The cleavage of the complex **22** to give the $H_2Si{=}O$ and $H_2C{=}CH_2$ products is also exothermic ($\Delta G°$ = –49.3 kcal/mol), however a significant energy barrier of 14.8 kcal/mol ($\Delta H°$) and 14.9 kcal/mol ($\Delta G°$) (at QCISD/6-31G**, 19.3 and 19.4 kcal/mol, respectively, at MP2/6-31G**) separates **22** from the products. The cleavage of **22** occurs in two steps: in the first step, one of the C—O bonds cleaves via transition state (TS) **26** to give the biradical intermediate **25**, which then fragments (via TS **27**) to produce

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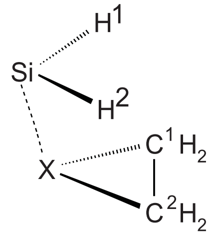
Table 2. Selected optimized geometry parameters at MP2/6–31G** and QCISD/6–31G** (in parenthesis) for intermediates and transition states in rxns. [2*a*]–[2*c*].[a]

Molecule	r(Si-X)	r(X-C_1)	r(X-C_2)	r(C_1-C_2)	<(Si-X-C_1)	<(Si-X-C_2)	<(Si-X-C_1-C_2)	<(H_1-Si-X-C_1)	<(H_1-Si-X-C_2)	<(H_2-Si-X-C_1)	<(H_2-Si-X-C_2)	<(Si-X-C_2-C_1)
O-zwitterion (**22**) C_1	203.6	146.0	146.1	146.3	116.7	120.3	–105.3	–41.6	27.8	–135.2	–65.8	111.2
	(205.7)	(145.5)	(145.6)	(146.6)	(117.5)	(120.6)	(–106.4)	(–41.2)	(29.1)	(–134.7)	(–64.4)	(111.4)
S-zwitterion (**23**) C_s	236	182.1	182.1	147.2	101.2	101.2	–95.0	108.1	156.8	–156.8	–108.1	95.0
	(239)	(182.8)	(182.8)	(147.6)	(101.9)	(101.9)	(–95.3)	(108.2)	(156.9)	(–156.9)	(–108.2)	(95.3)
Se-zwitterion (**24**) C_s	243.3	198.1	198.1	146.7	98.3	98.3	–93.3	110.9	154.9	–154.9	–110.9	93.3
O-transition state (**26**) C_1	177.3	146.3	188.9	144.5	121.3	130.5	–99.4	–31.3	29.4	–135.9	–75.2	118.6
	(181)	(143.8)	(185.5)	(145.8)	(119.1)	(128.7)	(–98.6)	(–39.1)	(22.0)	(–140.4)	(–79.3)	(117.9)
O-biradical intermediate (**25**) C_1	165.8	146.1	234.3	147.5	126.1	135.5	–93.1	–12.2	36.3	–134.9	–86.4	119.9
	(169.9)	(141.9)	(236.0)	(147.4)	(110.2)	(108.6)	(–99.0)	(–47.3)	(–9.0)	(–162.5)	(–124.2)	(94.1)
O-transition state (**27**) C_1	163.9	167.8	240.4	140.5	126.8	127.3	–103.0	27.5	71.5	–100.7	–56.6	104.4
	(162.8)	(169.6)	(244.4)	(140.3)	(124.1)	(121.7)	(–105.2)	(36.2)	(76.7)	(–92.0)	(–51.4)	(97.5)
S-transition state (**28**) C_s	212	212.9	212.9	139.7	120.8	120.8	–102.0	32.9	77.9	–77.9	–32.9	102.0
	(214.4)	(216.8)	(216.8)	(139.3)	(118.7)	(118.7)	(–100.7)	(33.2)	(76.2)	(–76.1)	(–33.2)	(100.7)
Se-transition state (**29**) C_s	224.5	222.4	222.4	140.3	119.6	119.6	–100.9	32.9	75.4	–75.4	–32.9	100.9

[a] For atom numbering see Scheme 4. Bond lengths are given in pm, angles in degrees.

Scheme 4. Definition of geometrical paramters for species **22**–**29**.



22-29

Table 3. Calculated enthalpies and Gibbs free energies (in parentheses) for various reactions (kcal/mol).

	ΔH_0° (ΔG_{298}°)	
Equation	MP2/6–31G**	QCISD/6–31G**
2*a*	–61.5 (–61.8)	–56.5 (–56.8)
2*b*	–44.9 (–45.2)	–44.2 (–44.4)
2*c*	–52.6 (–52.9)	
3*a*	–68.1	
3*b*	–50.3	
3*c*	–60.6	
4[a]	–58.9	

[a] At HF/6-31G**.

the desired silanone **6** (and ethylene). The biradical intermediate (**25**) lies higher in energy than **22** on both the Δ*H* and the Δ*G* surfaces (at QCISD)[2] and as the barrier for its cleavage is only ca. 2 kcal/mol, it is expected to have a very short lifetime.

These computational results are consistent with the only experimental kinetic study of the reaction of dimethylsilylene with oxirane (11*e*). Yet, the high value of the measured rate constant together with the observation of C_2H_4 formation, suggest that the calculated barrier of 14.9 kcal/mol (QCISD) separating **22** from **25** (i.e., TS **26**) is probably too high. This small theoretical–experimental discrepancy may result from real differences in the reactions of H_2Si (used in the calculations) and of $(CH_3)_2Si$ (used experimentally), or from errors in the calculations. B3LYP/6-31G**//B3LYP/6-31G** calculations indeed give a lower barrier of 10.4 kcal/mol for the conversion of **22** to **25** (Δ*H*° for the formation of **22** is –16.6 kcal/mol at this level). A more detailed theoretical study of the reaction of $(CH_3)_2Si$ with oxirane, as well as additional experiments are however required to reach a fully consistent theoretical–experimental picture of this reaction.

1. (b) The reaction of H_2Si with thiirane and selenirane

In contrast to the multistep fragmentation of the oxirane–silylene complex **22**, the fragmentation of the analagous S- and Se-complexes (**23** and **24**) to produce the desired products (silanethione **7** or silaneselone **8** (and ethylene), respectively) occurs in a single step via transition states **28** and

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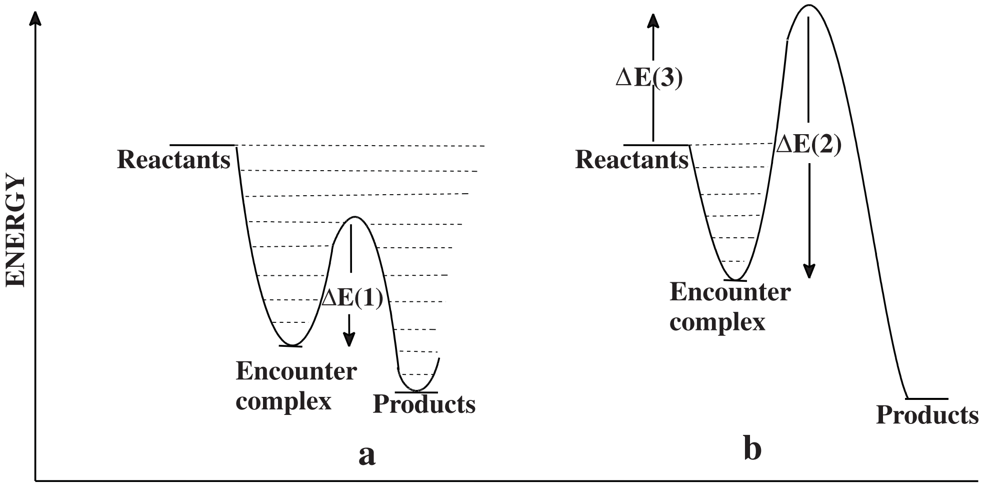
[2] At MP2/6–31G** **25** is slightly lower in energy than **22** (Table 1), but based on previous experience with biradicals (e.g., ref. 23) we prefer the QCISD/6–3IG** results.

Fig. 2. Schematic potential energy surfaces for an exothermic multi-step bimolecular gas-phase reaction: (*a*) the energy of the reactants is higher than that of the transition state for the conversion of the encounter-complex to products; (*b*) the energy of the reactants is lower than the energy of the transition state for the conversion of the encounter-complex to products.



29, respectively, in which the two C—X bonds are equally elongated.[3]

Reaction [2*b*] and each of its two steps are highly exothermic on both the Δ*H* and the Δ*G* surfaces (Fig. 4). Thus, Δ*H*° at 0 K for the overall reaction and for the first and second steps are: (QCISD, kcal/mol): –44.2, –16.8, and –27.4, respectively, and Δ*G*° = –44.4, –7.6, and –36.8, respectively. However, rxn. [2*b*], similarly to rxn. [2*a*], is spontaneous at 0 K but not at 298 K. The rate-determining step, as in rxn. [2*a*], is the cleavage of the intermediate silylene–thiirane complex **23**. The Gibbs free energy of activation for this step is calculated to be relatively high, ca. 15.0 kcal/mol at both QCISD and MP2 (Δ*H*° is very similar, 15.4 kcal/mol).[3] As the complexation energy released in the formation of **23** from the reactants of 7.6 kcal/mol is smaller than the energy required for its fragmentation (14.9 kcal/mol), **23** is predicted to be a long-lived entity even in the gas-phase. This conclusion applies even more strongly to the solution phase, where the energy gained by complexation can be speedily distributed to the environment and therefore it might be possible to observe **23** spectroscopically in matrices (the calculated vibrational frequencies of **23** are given in the supplementary material).

Reaction [2*c*] (Fig. 5) is the only reaction of the three reactions studied here in which no energy barrier exists between reactants and products either on the Δ*H* or on the Δ*G* surfaces (i.e., the reaction is of type (*a*) in Fig. 2). Reaction [2*c*] in contrast to rxns. [2*a*] and [2*b*], is therefore predicted to occur spontaneously in the gas-phase, as the barrier for the fragmentation of the silylene–selenirane intermediate **24** (Δ*G*° = 7.5 kcal/mol) is significantly lower than the energy released (Δ*G*° = –21.8 kcal/mol) upon its formation (Fig. 5). Reaction [2*c*] is predicted to be very facile also in solution as the barrier for the fragmentation of complex **24** is small, only 7.5 kcal/mol.

In summary, the calculations show that rxns. [2*a*]–[2*c*] are highly exothermic, both on the Δ*H* and Δ*G* energy surfaces, in the range of –44 – –56 kcal/mol (QCISD/6-31G**) depending on the heteroatom X of the reactant three-membered ring. All reactions proceed via intermediate $H_2Si\cdots XC_2H_4$ donor–acceptor complexes which are formed spontaneously. These complexes are quite stable kinetically (less so for

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[3] It is noteworthy that the synchronous single-step fragmentation of the $H_2Si\cdots XC_2H_4$ encounter-complexes, **22–24**, to the corresponding $H_2Si{=}X$ and ethylene is formally a "symmetry-allowed" reaction in a "linear-type" process (see ref. 24). Thus, assuming a linear-type process with C_s-symmetry the relevant occupied orbitals of the reactant (**22**) are: (*i*) the two σ(C—X) bonds — one symmetric (S) and one *anti*-symmetric (A); (*ii*) the Si···X bond (S); (*iii*) and the silylene lone-pair (S). These orbitals correlate with those of the ground state orbitals of the products, $H_2C{=}CH_2$ + $CH_2{=}X$, i.e., σ(C—X) (S), π(C=X) (S), π(C=C) (S), and the lone-pair on O (A). A close analogy to rxns. [2*a*]–[2*c*] is the abstraction of NR from *N*-alkylaziridines by dichlorocarbenes producing olefins in which the relative configuration of the substituents is retained, indicating a synchronous symmetry-allowed process (see for example ref. 25). However, a closer examination of the reaction reveals that the fragmentation step has, to some extent a "symmetry-forbidden" contribution due to the very high polarity of the $H_2Si{=}X$ molecules which are better described as $H_2Si^+{—}X^-$ (the calculated charges on X are: –0.96, –0.55, –0.46 for X = O, S, Se, respectively). To better understand this point it is more convenient to analyze the fragmentation reaction in the reverse direction, i.e., as an addition reaction of $H_2Si^+{—}X^-$ to $CH_2{=}CH_2$. Such a reaction is a symmetry-forbidden $\pi 2s + \omega 2s$ reaction. In agreement with this analysis, the fragmentation reactions of **22–24**, although highly exothermic, have significant activation barriers and for X = O, the preferred reaction path is indeed nonconcerted, i.e., it proceeds via a two-step mechanism, as expected for a symmetry–forbidden reaction (a C_s species having two imaginary frequencies and closely corresponding to TS **28** for X = S and to TS **29** for X = Se, is 5.9 kcal/mol higher in energy than the biradicaloid TS **26**) The contribution of the polarity to the degree of symmetry-forbiddeness of the fragmentation reactions is smaller for X = S and Se than for X = O, due to the lower polarity of $H_2Si{=}S$ and $H_2Si{=}Se$ relative to $H_2Si{=}O$, and with these chalcogonites fragmentation occurs in a single step. Another factor contributing to the significant barriers of the fragmentation step is the high degree of electron reorganization required along the fragmentation process (see for example ref. 26).

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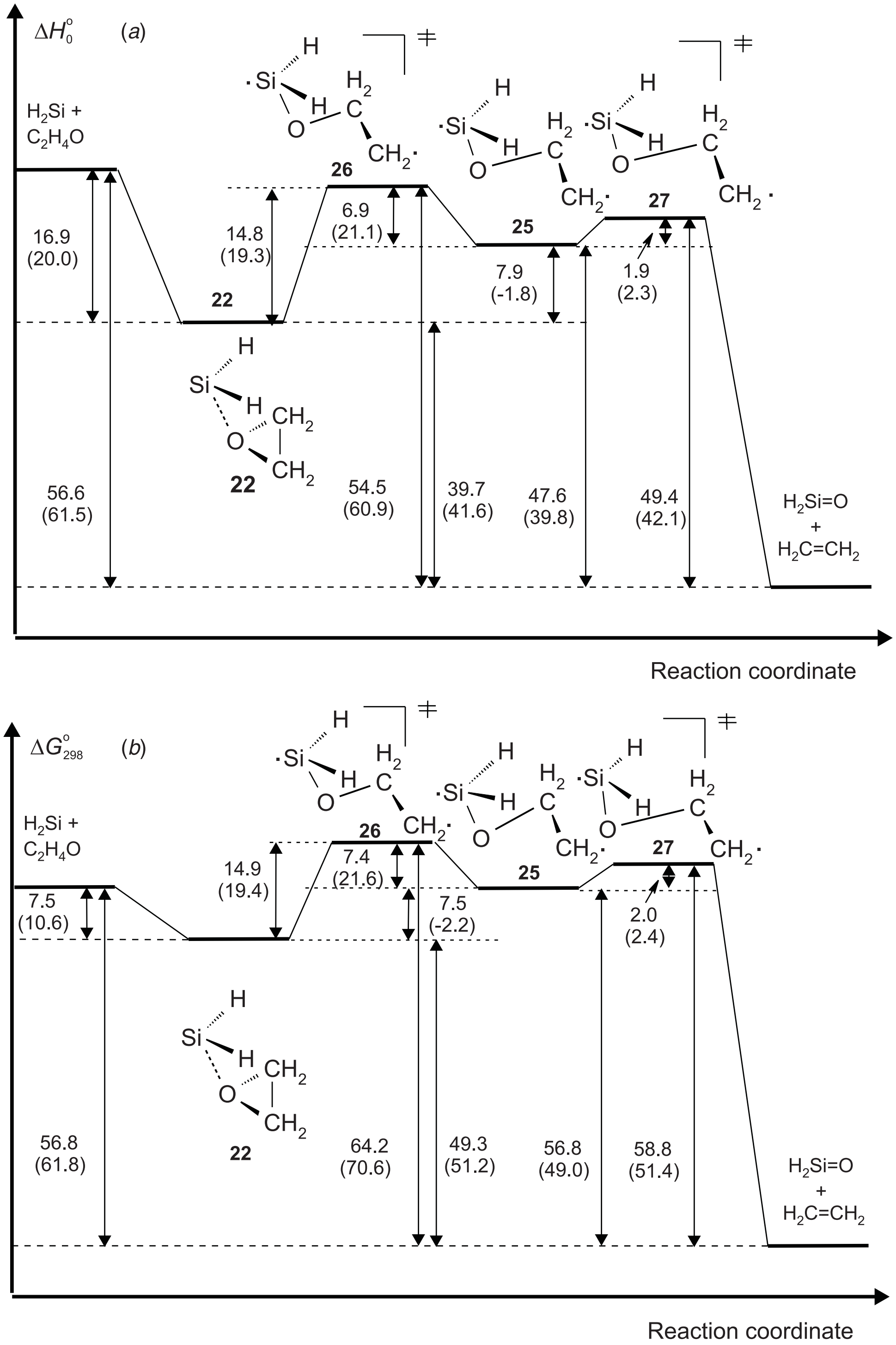
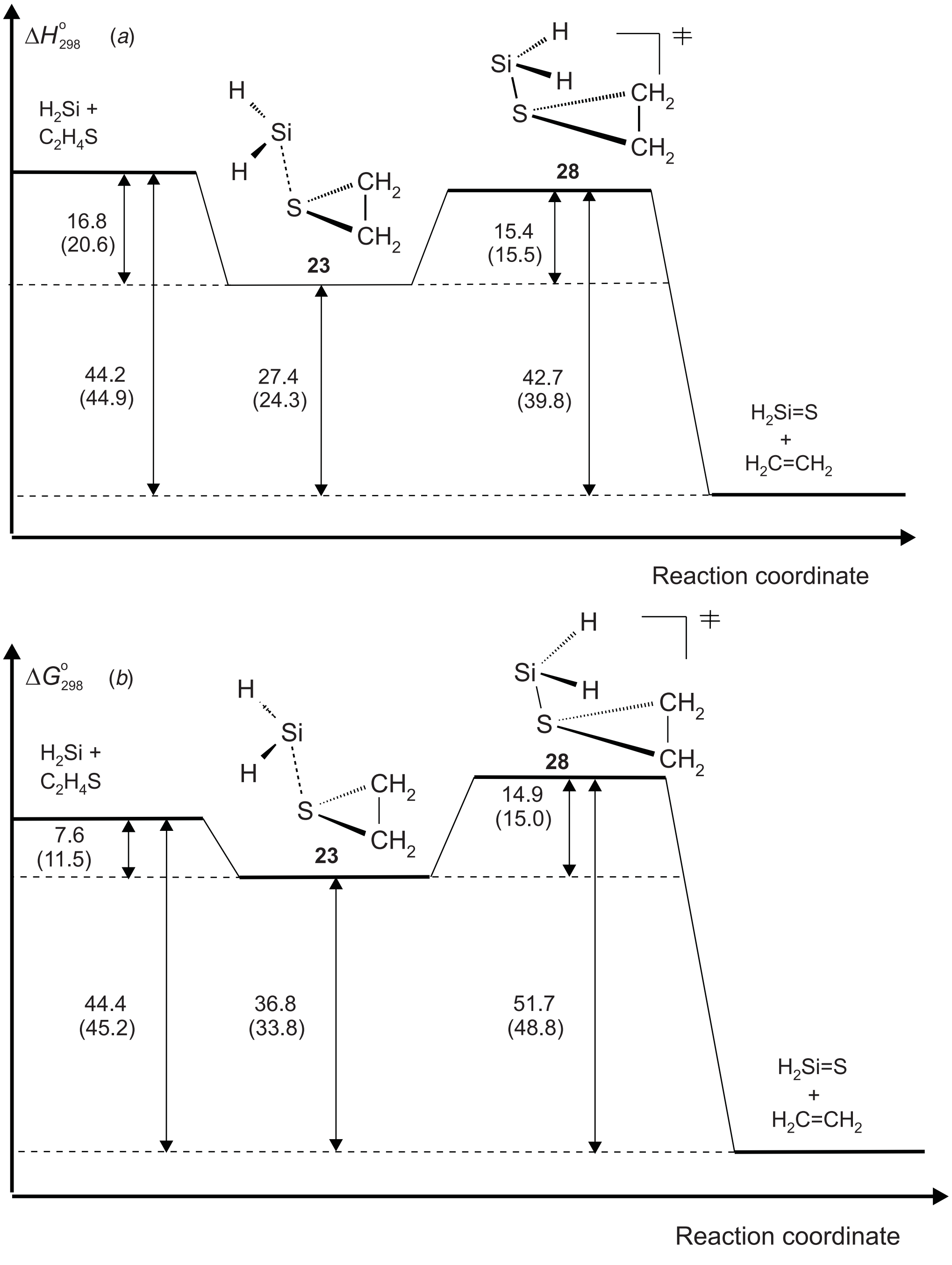
Fig. 3. Calculated reaction scheme for eq. [2*a*] at QCISD/6–31G** and at MP2/6–31G** (values in parenthesis). The figure is drawn according to the QCISD/6–31G** values and the relative energies are given in kcal/mol. (*a*) Reaction enthalpies. (*b*) Gibbs free energies at 298 K.



X = Se) and according to the calculations should be detectable in low-temperature matrices. The cleavage of these complexes is also highly exothermic and in the gas-phase at 0 K it is also spontaneous (i.e., represented by a PES of type (*a*) in Fig. 2). However, at 298 K, even in the gas-phase, the cleavage of the donor–acceptor complex is spontaneous only for X = Se. For X = O and X = S, a significant barrier (ΔG = 7.4 kcal/mol for both reactions) exists and the energy gained in the complexation step is not sufficient to overcome the barrier separating the complex from the products. In solution, where the silylene–XC_2H_4 complexes may have the possibility to relax, the barriers which have to be overcome are larger and become quite significant, i.e., 14.9 kcal/mol for both reactions (at QCISD).

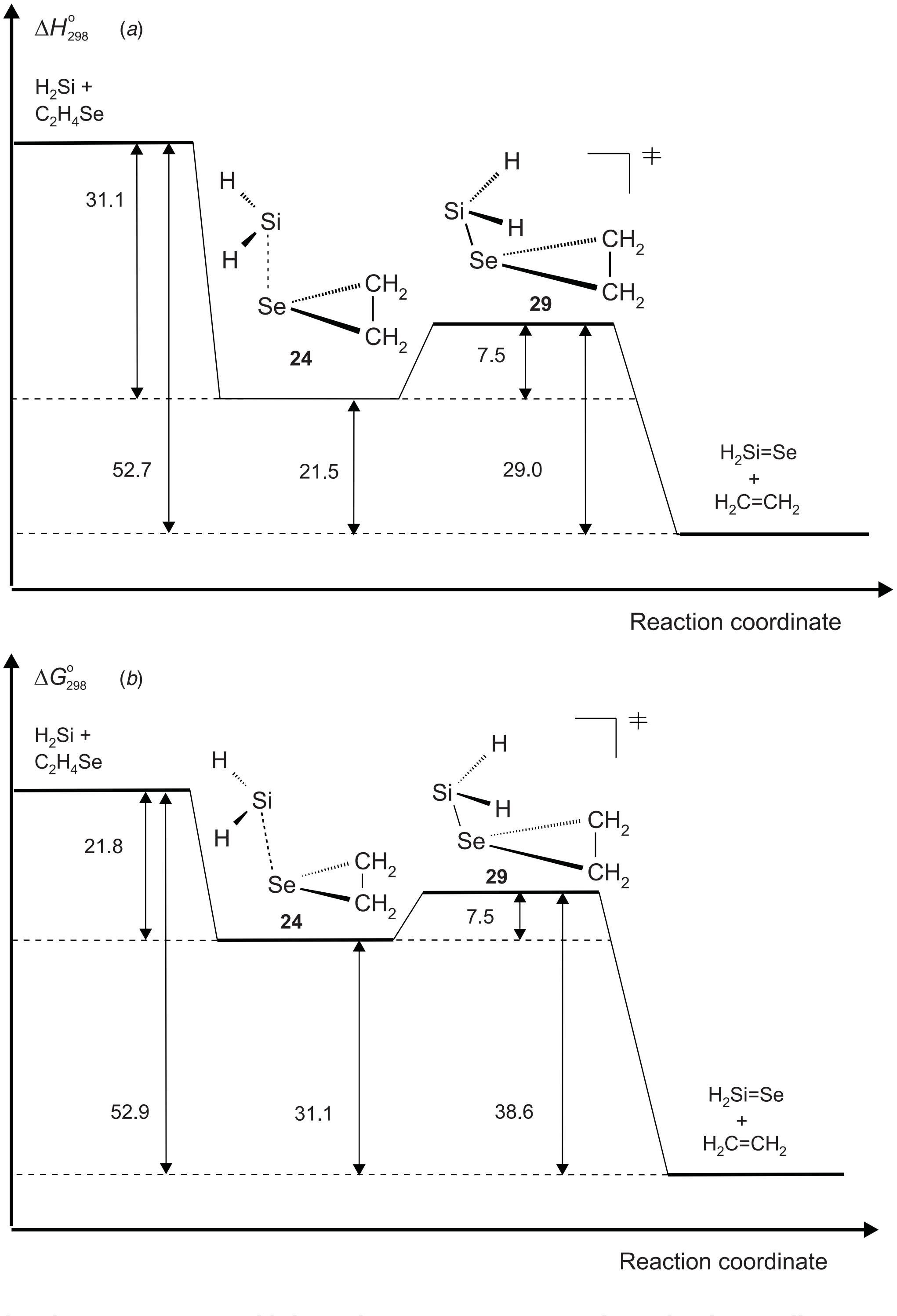
Fig. 4. Calculated reaction scheme for eq. [2*b*] at QCISD /6–31G** and at MP2/6–31G** (values in parenthesis). The figure is drawn according to the QCISD/6–31G** values and the relative energies are given in kcal/mol. (*a*) Reaction enthalpies. (*b*) Gibbs free energies at 298 K.



1. (c) The silatane route

Barton (11*b*) and Barton and Goure (11*c*), who studied experimentally the reaction of dimethylsilylene with cyclohexane oxide, pointed out that an alternative mechanism to that shown in Fig. 3, i.e., via the corresponding silaoxetanes (see path A in Scheme 2), could not be excluded. To evaluate the viability of this mechanistic possibility, we have calculated the "silatane route" for the reaction of H_2Si with **9**–**11**, shown in Scheme 5. Our results reveal that the rearrangement of **22** to **30***a* is very sluggish since the calculated barrier $E_a(1)$ is 32.0 kcal/mol. Unfortunately, we could not locate the corresponding transition states connecting the silylene complexes **23**–**24** with the corresponding silatanes **30b**–**30c**, and thus could not compare directly these barriers ($E_a(1)$) with the corresonding barriers for fragmentation of the complexes **23**–**24** to the corresponding H_2Si=X + C_2H_4, $E_a(4)$ in Scheme 5 ($E_a(4)$ are the barriers to the fragmentation of **22**–**24** given in Figs. 3*a*–3*c*, respectively). However, even without this direct comparison the calculations (at the MP2/6-31G**//MP2/6-31G** level), show clearly (Table 4)

Fig. 5. Calculated reaction scheme (kcal/mol) for eq. [2*c*] at MP2/6–31G**. The relative energies are given in kcal/mol. (*a*) Reaction enthalpies. (*b*) Gibbs free energies at 298 K.



that in solution the silatane route is not a likely mechanism for the production of $H_2Si{=}X$. Thus, the silatanes **30a–30c,** even if formed in the reaction, are significantly more stable than the final products of rxn. [2] (i.e., by 31.5, 29.8, 29.9 kcal/mol for X = O, S, and Se, respectively (see $\Delta H(2)$ values in Table 4). Furthermore, the cleavage of the silatanes involves additional activation barriers ($E_a(-2)$ values in Table 4) of 9.9, 11.4, and 8.6 kcal/mol for X = O, S, Se, respectively, so that the overall activation barriers, $E_a(2)$, for the cleavage of the silatanes **30a**–**30c** to the corresponding $H_2Si{=}X$ are 41.4, 41.2, and 38.4 kcal/mol, respectively, (Table 4). Thus, if the silatanes were indeed formed as intermediates in the reactions of silylenes with chalcogenide three-membered rings, they would not be expected to extrude $H_2Si{=}X$ under the reaction conditions used in the literature experiments and therefore they should have been detected experimentally. At the moment experiments are available only for X = O and in agreement with the above theoretical analysis, silaoxetanes were not detected in solution experiments (11*a*–11*c*, 21)[4]. Also, in gas-phase reactions the silatanes are not expected according to the calculations to be observed experimentally, as the energy released in their production Δ*H*(1), far exceeds the energy, $E_a(2)$, required for their fragmentation. This is in agreement with the available gas-phase experiments (11*e*, 21)[4].

Attempts to locate a reaction path connecting directly the reactants with the corresponding silatanes, i.e., a direct insertion of the silylene into the strained C—X bond of the XC_2H_4 molecule (a reaction which is exothermic (Δ*H*(3) in Scheme 5) by –97.7, –79.3, and –87.1 kcal/mol (MP2/6–31G**) for X = O, S, and Se, respectively) have failed, but we believe that these pathways are higher in energy than via the silylene–XC_2H_4 complexes.

Our computational results combined with the fact that silaoxetanes were not observed experimentally in these reactions (11) strongly support the conclusion that silaoxetanes are not involved as intermediates in the reactions of silylenes with chalcogenide three-membered rings. The calculations also show that silatanes are not good precursors for the production of Si=X multiple bonds (e.g., via pyrolysis), because the activation barriers for their fragmentation, $E_a(2)$, are high, ca. 38–41 kcal/mol, requiring relatively high reaction temperatures.

2. Reactions of dimethylsilylene and diphenylsilylene with chalcogenide three-membered rings

Do the calculations for the parent H_2Si discussed above apply also to silylenes, which experimentally are used more widely than H_2Si, such as dimethylsilylene and diphenylsilylene? To answer this question we have calculated the reaction enthalpies of rxn. [3] (at MP2/6–31G**//MP2/6–31G**) and of rxn. [4] (at HF/6–31G**//HF/6–31G**). The calculated reaction energies (Table 3) are quite similar to those obtained for the parent rxns. [2*a*]–[2*c*] and although a full scan of the PES was not carried out, this result suggests that alkyl- and aryl-substituted silylenes can also serve as precursors for producing the desired R_2Si=X compounds. Of particular interest is the computational prediction that even with the relatively stable Ph_2Si the reaction with oxirane to give Ph_2Si=O is still highly exothermic, i.e., by –58.9 kcal/mol. This suggests that it might be possible to use even sterically protected silylenes, such as Mes_2Si and even Tbt_2Si, to produce sterically stabilized silanones, e.g., Mes_2Si=O and Tbt_2Si=O. We encourage experimentalists to test this suggestion.

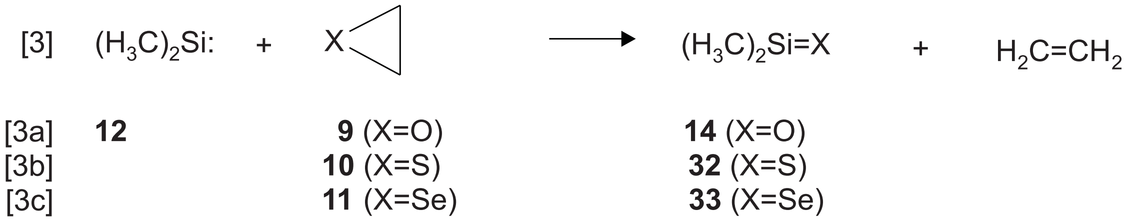
Table 4. Calculated enthalpies and activation energies (kcal/mol) at MP2/6–31G**//MP2/6–31G** for the silatane route (Scheme 5).

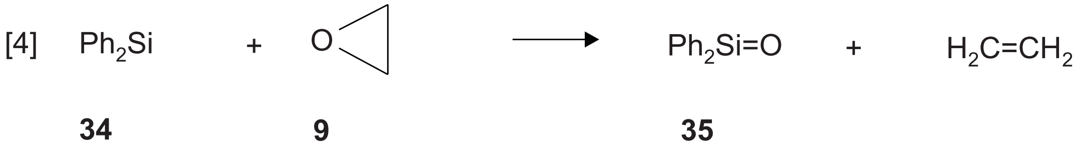
X	Δ*H*(1)	Δ*H*(2)	$E_a(2)$	$E_a(-2)$
O	–73.1	31.5	41.4	9.9
S	–54.2	29.8	41.2	11.4
Se	–51.4	29.9	38.5	8.6

Equilibrium geometries

The differences between the QCISD and the MP2 calculated geometries are relatively small (see Fig. 1 and Table 2), and the discussion below is based on the QCISD geometries (except for X = Se, where only MP2 values are available) which are believed to be more reliable.

The doubly bonded compounds: silanone (**6**), silanethione (**7**), and silaneselone (**8**) are all planar, i.e., have C_{2v} symmetry. The calculated Si=X bond lengths (pm) of: 153.8 (X = O), 195.4 (X = S), and 207.0 (X = Se) are all significantly shorter (by ca. 8–9%) than the corresponding Si—X single





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[4] For X = O, the silaoxetane **30a** can be formed from the silylene–oxirane complex **22** via ring-closure of the biradical **25**. This ring-closure requires rotation around the Si—O and C—C bonds in **25**. The fact that a silaoxetane was not observed experimentally (11*a*–11*c*, 11*e* indicates that the fragmentation of **25** to H_2Si=O and H_2C=CH_2 is faster than its ring closure to **30a**. This is reasonable, as the activation barrier for the fragmentation of **25** is only ca. 2 kcal/mol and it essentially involves only elongation of the C—O bond, while ring-closure to **30a** requires rotation around two bonds, reducing the dynamic probability of this process (for a discussion of the rates of rotation around C—C bonds in biradicals, see for example ref. 21). The actual substituents used in the experiments, which are significantly larger than H used in the calculations, may further slow down the ring-closure relative to fragmentation. The fact that silaoxetanes were not observed experimentally implies that the free energy of activation for the ring-closure of **25** is by at least 3 kcal/mol higher in energy than that for its fragmentation. For X = S and Se we could not locate the transition state which separates the S–silylene and Se–silylene complexes (**23** and **24**, respectively) from the corresponding silatanes, **30b** and **30c**. We assume that also in these cases these barriers are higher than the corresponding fragmentation barriers to the products (15.4 and 7.5 kcal/mol, respectively), but this point will have to be rechecked when such experiments will become available.

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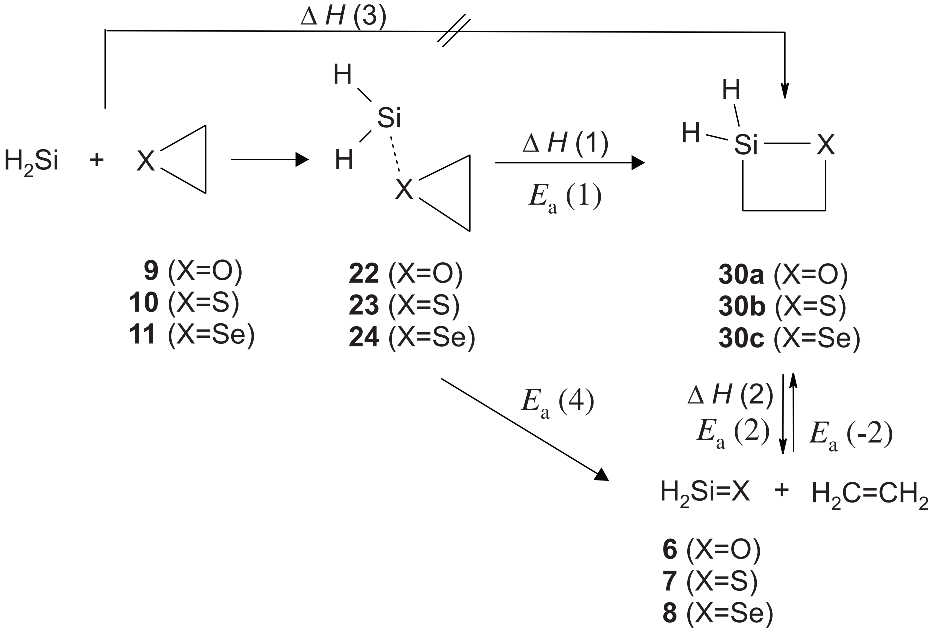
Scheme 5. The silatane route.



bond distances, (166.7, 214.3, 226.6 pm, respectively in H_3SiXH), indicating the multiple bonding nature of the Si=X bond in these molecules. The calculated (H-Si-H) bond angles are: 111.5° (X = O), 110.2° (X = S), and 109.6° (X = Se) and the Si—H bond lengths in all species are 147.3 pm. The calculated QCISD geometry of silanone **6** agrees well with the recently measured experimental values (8*b*) (r(Si=O) = 151.5 pm, r(Si—H) = 147.2 pm, < (H-Si-H) = 112.0°) as well as with the best available calculated geometry at CCSD/TZ2P(f,d)//CCSD/TZ2P(f,d) (8*c*). Substitution of the hydrogens in H_2Si=X by two methyl groups has a minor effect on the geometry of the Si=X.

The calculated charges and geometries of the silylene–XC_2H_4 complexes (Table 2) are consistent with the description of these species as involving a modest donor–acceptor interaction between one of the lone pairs of X (donor) and the vacant 3*p*(Si) orbital (acceptor).[5] Thus, in the encounter complexes **22**–**24**, the calculated total charge transferred from C_2H_4X to the SiH_2 unit (using the Natural Population Analysis at MP2(full)/6–31G**) is: 0.15 el. in **22**, 0.31 el. in **23**, and 0.34 el. in **24**. Consistent with the modest charge transfer is the fact that the Si···X distances in the complexes **22**–**24** are quite long, r(Si—X) = 205.7 (X = O), 239.0 (X = S), and 243.3 (X = Se) pm, in comparison with the corresponding Si—X single bonds in H_3SiXH: 166.7 (X = O), 214.3 (X = S), and 226.6 (X = Se) pm. Similarly, the C—X bond lengths in the complexes are only slightly elongated (by 1–2 ppm) compared to those calculated for the corresponding three-membered ring precursors. The silylene is tilted above the three-membered ring; the Si-X-Y bond angle (where Y is the center of the C—C bond) is 124° for **22,** and ca. 102° for **23** and **24**. Rotation of the silylene around the Si···X axis is facile (barriers of 0.6–2 kcal/mol), with **22** preferring the "inside" conformation (i.e., where the ∠HSiXC dihedral angle is ca. 0°), while **23** and **24** are more stable in the "outside" conformation (e.g., ∠HSiXC is ca. 180°). Although, the geometrical parameters of **22**–**24** indicates a relatively weak complexation, the calculated complexation energies show that these complexes are bound quite strongly; i.e., by 20.0, 20.6, and 31.1 kcal/mol for X = O, S, Se, respectively, (at MP2). This apparent dichotomy between the geometries and the complexation energies reflects the high energies of the Si—X bonds (22).

The transition states for the concerted fragmentation of the silylene–XC_2H_4, X = S, Se intermediates (**28** and **29**, respectively) are structurally similar to those of the corresponding silylene–XC_2H_4 complexes (**23** and **24**, respectively), but they have much shorter Si···X distances (r(Si—X) = 214.4 and 224.5 pm), much longer C—X bonds (r(C—X) = 216.8 and 222.4 pm), significantly shorter C—C bonds (ca. 140 pm) and significantly wider Si-X-C bond angles (ca. 120°), compared to those parameters in the corresponding complexes. Actually, the r(Si—X) distances in **28** and **29** are very close to those of the corresponding Si—X single bonds (214.3 and 226.6 pm for X = S and Se, respectively) and these transition states can be described as occurring relatively "late" along the fragmentation reaction coordinate.

In the silylene–oxirane reaction the intermediate complex **22** undergoes cleavage in two steps: (*i*) first only one of the C—O bonds breaks (via TS **26**) to give the biradical complex **25**; (*ii*) followed by cleavage of the second C—O bond (TS **27**) to give H_2Si=O and ethylene. Along the progression: **22** → **26** → **25** → **27** → **6**, the Si—O bond length is gradually shortened (205.7, 181.0, 169.9, 162.8, and 153.8 pm respectively) and the C—O bond length is gradually elongated (143.2 (**9**), 145.6 (**22**), 185.5 (**26**), 236.0 (**25**), and 244.4 (**27**), pm). The largest differences between the QCISD and MP2 geometries are found for the *biradical* **25** (Table 2).

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[5] Silylene–XR_2 complexes are often referred to in the literature as "zwiterionic." According to the calculations this description is not justified and we prefer to refer to them as donor–acceptor complexes.

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Conclusions

High level ab initio calculations for the reactions between silylene and oxirane (**9**), thiirane (**10**), and selenirane (**11**) which are possible routes to Si=X double bonds (X = O, S, Se, eqs. [2*a*]–[2*c*]), show that these reactions are highly exothermic ($\Delta H°$ = –61.5, –44.9, and –52.7 kcal/mol for X = O, S, Se, respectively at MP2/6–31G**) and in the gas-phase at 0 K they are also spontaneous. The first step of these reactions involves the barrierless formation of a donor–acceptor complex between the silylene and the X atom of the precursor, C_2H_4X. The reaction steps which follow depend on X. For X = O, fragmentation of the silylene–C_2H_4X complex **22** proceeds in two steps via a biradical intermediate. In contrast, fragmentation of the S (**23**) and the Se (**24**) complexes occurs in a single step. At 298 K in the gas-phase, the contributions of entropy lead for X = O and S, to a small energy barrier (ΔG) of 7.4 kcal/mol on the path between the silylene–XC_2H_4 complex and the products, but for X = Se the reaction is spontaneous also at 298 K. In solution, a barrier of 7.5 kcal/mol separates the silylene complexes from the products also for X = Se and this barrier is somewhat higher (14.9 kcal/mol) for X = O, and S. However, these barriers can be easily surmounted, making these reactions synthetically attractive.

In conclusion, the computational results suggest that the reaction of silylenes with chalcogenide three-membered ring compounds (eq. [1]) is indeed a viable route for the preparation of compounds with a Si=X double-bond (X = O, S, Se), both in the gas-phase and in solution. We call for an experimental testing of this prediction.

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Supplementary material

Tables of calculated vibrational frequencies for the silylene–XC_2H_4 complexes **22**, **23**, and **24**. A copy of the supplementary material may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2 (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically).

References

1. (*a*) G. Raabe and J. Michl. *In* The chemistry of organic silicon compounds. *Edited by* S. Patai and Z. Rappoport. Wiley, Chichester, U.K. 1989. Chap. 17; (*b*) Y. Apeloig. *In* The chemistry of organic silicon compounds. *Edited by* S. Patai and Z. Rappoport. Wiley, Chichester, U.K. 1989. Chap. 2; (*c*) N. Tokitoh and R. Okazaki. *In* The chemistry of organic silicon compounds. Vol. 2. *Edited by* Z. Rappoport and Y. Apeloig. Wiley, Chichester, U.K. 1998. Chap. 17.
2. (*a*) H. Suzuki, N. Tokitoh, S. Nagase, and R. Okazaki. J. Am. Chem. Soc. **116**, 11578 (1994); (*b*) H. Suzuki, N. Tokitoh, R. Okazaki, S. Nagase, and M. Goto. J. Am. Chem. Soc. **120**, 11096 (1998).
3. N. Tokitoh, T. Sadahiro, N. Takeda, and R. Okazaki. The 12th international symposium on organosilicon chemistry. Sendai, Japan, May 23–28, 1999. Abstract 4A-23.
4. (*a*) R. Koppe and H.Z. Schnockel. Z. Anorg. Allg. Chem. **607**, 41 (1992); (*b*) V. Lefevre and J.L. Ripoll. Phosp. Sulfur Silicon, **120**, 37 (1997).
5. (*a*) D.P. Thompson and P. Boudjouk. J. Chem. Soc. Chem. Commun. 1466 (1987); (*b*) P. Boudjouk, S.R. Bahr, and D.P. Thompson. Organometallics, **10**, 778 (1991).
6. (*a*) P. Arya, J. Boyer, F. Carre, R. Corriu, G. Lanneau, J. Lapasset, M. Perrot, and C. Priou. Angew. Chem. Int. Ed. Engl. **28**, 1016 (1989); (*b*) J. Belzner, I. Heiko, B.O. Kneisel, and R. Herbst-Irmer. Chem. Ber. **129**, 125 (1996).
7. (*a*) R. Withnall and L. Andrews. J. Phys. Chem. **89**, 3261 (1985); (*b*) R.J. Glinski, J.L. Gole, and D.A. Dixon. J. Am. Chem. Soc. **107**, 5891 (1985); (*c*) R. Withnall and L. Andrews. J. Phys. Chem. **92**, 594 (1989), and refs. therein.
8. (*a*) R. Srinivas, D.K. Boehme, D. Suelzle, and H. Schwarz. J. Phys. Chem. **95**, 9836 (1991); (*b*) S. Bailleaux, M. Bogey, C. Demuynck, J. Destombes, and A. Walters. Chem. Phys. **101**, 2729 (1994); (*c*) B. Ma and H.F. Schaefer, III. J. Chem. Phys. **101**, 2734 (1994); (*d*) M. Bogey, B. Delcroix, A. Walters, and J.C. Guillemin. J. Mol. Spectrosc. **175**, 421 (1996); (*e*) B. Ma, N.L. Allinger, and H.F. Schaefer, III. J. Chem. Phys. **105**, 5731 (1996).
9. (*a*) T. Kudo and S. Nagase. J. Phys. Chem. **88**, 2833 (1984); (*b*) T. Kudo and S. Nagase. Chem. Phys. Lett. **128**, 507 (1986); (*c*) T. Kudo and S. Nagase. J. Am. Chem. Soc. **107**, 2589 (1985); (*d*) M.S. Gordon and L.A. Pederson. J. Phys. Chem. **94**, 5527 (1990); (*e*) J. Kapp, M. Remko, P. von R. Schleyer. J. Am. Chem. Soc. **118**, 5745 (1996); (*f*) T. Kudo, F. Hashimoto, and M.S. Gordon. J. Comput. Chem. **17**, 1163 (1996); (*g*) J.M.L. Martin. J. Phys. Chem. **102**, 1294 (1998); (*h*) J. Koput, S. Carter, and N.C. Handy. Chem. Phys. Lett. **301**, 1 (1999).
10. (*a*) T. Kudo and S. Nagase. Organometallics, **5**, 1207 (1986); (*b*) P.J. Bruna and F. Grein. Chem. Phys. **165**, 265 (1992); (*c*) M.W. Schmidt, P.N. Truong, and M.S. Gordon. J. Am. Chem. Soc. **109**, 5217 (1987); (*d*) L. Nyulaszi, A. Belghazi, S.K. Szetsi, T. Veszpremi, J. Heinicke. THEOCHEM. **119**, 73 (1994).
11. (*a*) D. Tzeng and W.P. Weber. J. Am. Chem. Soc. **102**, 1451 (1980); (*b*) T.J. Barton. Pure Appl. Chem. **52**, 615 (1980); (*c*) W.F. Goure and T.J. Barton. J. Organomet. Chem. **199**, 33 (1980); (*d*) W. Ando, M. Ikeno, Y. Hamada. J. Chem. Soc. Chem. Commun. 621 (1981); (*e*) J.E. Baggott, M.A. Blitz, H.M. Frey, P.D. Lightfoot, and R. Walsh. Int. J. Chem. Kinet. **24**, 127 (1992).
12. (*a*) D.C. Dittmer. *In* Comprehensive heterocyclic chemistry. Vol. 7, Part 5. *Edited by* A.R. Katritzky and C.W. Rees. Pergamon Press, Oxford. 1984. Chap. 5; (*b*) Yu V. Razskazovskii, M.V. Roginskaya, and M.Ya. Mel'nikov. J.Organomet. Chem. **486**, 249 (1995).
13. (*a*) W. Ando, Y. Kumamoto, and N. Tokitoh. Tetrahedron Lett. **28**, 2867 (1987); (*b*) W. Ando, Y. Kumamoto, and N. Tokitoh. J. Phys. Org. Chem. **1**, 317 (1988); (*c*) S. Watanabe, T. Kawashima, and R. Okazaki. Chem. Lett. 1289 (1994).
14. W.J. Hehre, L. Radom, P.v.R. Schleyer, and J.A. Pople. Ab initio molecular orbital theory. Wiley, New York. 1986.

15. (*a*) M. Head-Gordon, J.A. Pople, and M.J. Frisch. Chem. Phys. Lett. **153**, 503 (1988); (*b*) M.J. Frisch, M. Head-Gordon, and J.A. Pople. Chem. Phys. Lett. **166**, 275 (1990); (*c*) M.J. Frisch, M. Head-Gordon, and J.A. Pople. Chem. Phys. Lett. **166**, 281 (1990).
16. J.A. Pople, M. Head-Gordon, and K. Raghavachari. J. Chem. Phys. **87**. 5968 (1987).
17. M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.J.P. Stewart, M. Head-Gordon, C. Gonzalez, and J.A. Pople. Gaussian 94. Gaussian, Inc., Pittsburgh, Pa. 1995.
18. (*a*) W.J. Hehre, R. Ditchfield, and J.A. Pople. J. Chem. Phys. **56**, 2257 (1972); (*b*) P.C. Hariharan and J.A. Pople. Theor. Chim. Acta, **28**, 213 (1973); (*c*) M.S. Gordon, J.S. Binkley, J.A. Pople, W.J. Pietro, and W.J. Hehre. J. Am. Chem. Soc. **104**, 2797 (1982); (*d*) M.M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. DeFrees, and J.A. Pople. J. Chem. Phys. **77**, 3654 (1982).
19. (*a*) C. Gonzalez and H.B. Schlegel. J. Chem. Phys. **90**, 2154 (1989); (*b*) C. Gonzalez and H.B. Schlegel. J. Phys. Chem. **94**, 5523 (1990).
20. P.P. Gaspar and R. West. *In* The chemistry of organic silicon compounds. Vol. 2. *Edited by* Z. Rappoport, and Y. Apeloig. Wiley, Chichester, U.K. 1998. Chap. 43.
21. C. Doubleday, M. Nedel, K.N. Houk, D. Thweatt, and M. Page. J. Am. Chem. Soc. **121**, 4720 (1999), and refs. therein.
22. R. Walsh. *In* The chemistry of organic silicon compounds. Vol. 2. *Edited by* Z. Rappoport and Y. Apeloig. Wiley, Chichester, U.K. 1998. Chap. 4.
23. K. Raghavachari, J.A. Pople, and M. Head-Gordon. J. Phys. Chem. **94**, 5579 (1990).
24. R.B. Woodward and R. Hoffmann. The conservation of orbital symmetry. Verlag Chemie, Weinheim, Germany. 1971.
25. Y. Hata and M. Watanabe. J. Am. Chem. Soc. **95**, 8450 (1973); Tetrahedron Lett. **46**, 4659 (1972).
26. S. Shaik and A. Shurki. Angew Chem. Int. Ed. Engl. **39**, 586 (1999).