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Ab Initio Study of Some Methylene and Silylene Insertion Reactions

David R. Gano,[†] Mark S. Gordon,[*,‡] and Jerry A. Boatz[§]

Contribution from the Departments of Chemistry, Minot State University, Minot, North Dakota 58701, North Dakota State University, Fargo, North Dakota 58105, and University of Utah, Salt Lake City, Utah 84112. *Received September 21, 1989*

Abstract: The theoretical barriers and reaction energetics have been determined, using ab initio calculations at the MP4/6-31G(d) level, with 3-21G* geometries, for the insertions of methylene and silylene into the X–Y bonds of ethane, methylsilane, disilane, and cyclopropane and into the X–H bonds of disilane and ethane. A correlation was observed between barrier heights and lengths of substrate bonds. The largest barriers were observed for methylene and silylene inserting into the C–C bonds of ethane. The barriers became successively lower for the C–Si and Si–Si bonds. Steric interactions thus appear to be a major factor in determining barrier heights. The observed barriers for silylene and methylene inserting into the strained C–C bonds of cyclopropane were approximately 40 kcal/mol less than those for the analogous unstrained compounds.

I. Introduction

The differences and similarities between carbon and silicon have intrigued chemists for years. Out of this vast area of knowledge the chemistry of methylene (CH_2) versus silylene (SiH_2) has been of continuing interest. These reactive intermediates are produced by pyrolysis or photodecomposition of organic, organosilicon, or silicon compounds.[1] Previous papers have dealt with both thermal and photochemical dissociations of parent compounds to yield methylene[2-4] and silylene,[3,5,6] with the effects of substituents on the singlet–triplet splittings in CH_2 and SiH_2,[7] with the isomerizations of carbenes and silylenes to their formally doubly bound isomers,[2,3,5,8] and with methylene vs silylene reactivity.[9] With regard to the latter, the singlet states of these very reactive intermediates prefer insertion into available bonds, particularly X–H bonds.

In recent years experimental and theoretical studies have focused on several reactions. The insertion of methylene into H–H and C–H bonds has been predicted theoretically[10] to occur with no barrier, in good agreement with experimental[11] results. The barrier for the insertion into the C–H bond was calculated by using third-order many-body perturbation theory (MP3)[12] and the 6-31G(d) basis set,[13] at the 3-21G[14] geometries (denoted

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[†] Minot State University.
[‡] North Dakota State University.
[§] University of Utah.

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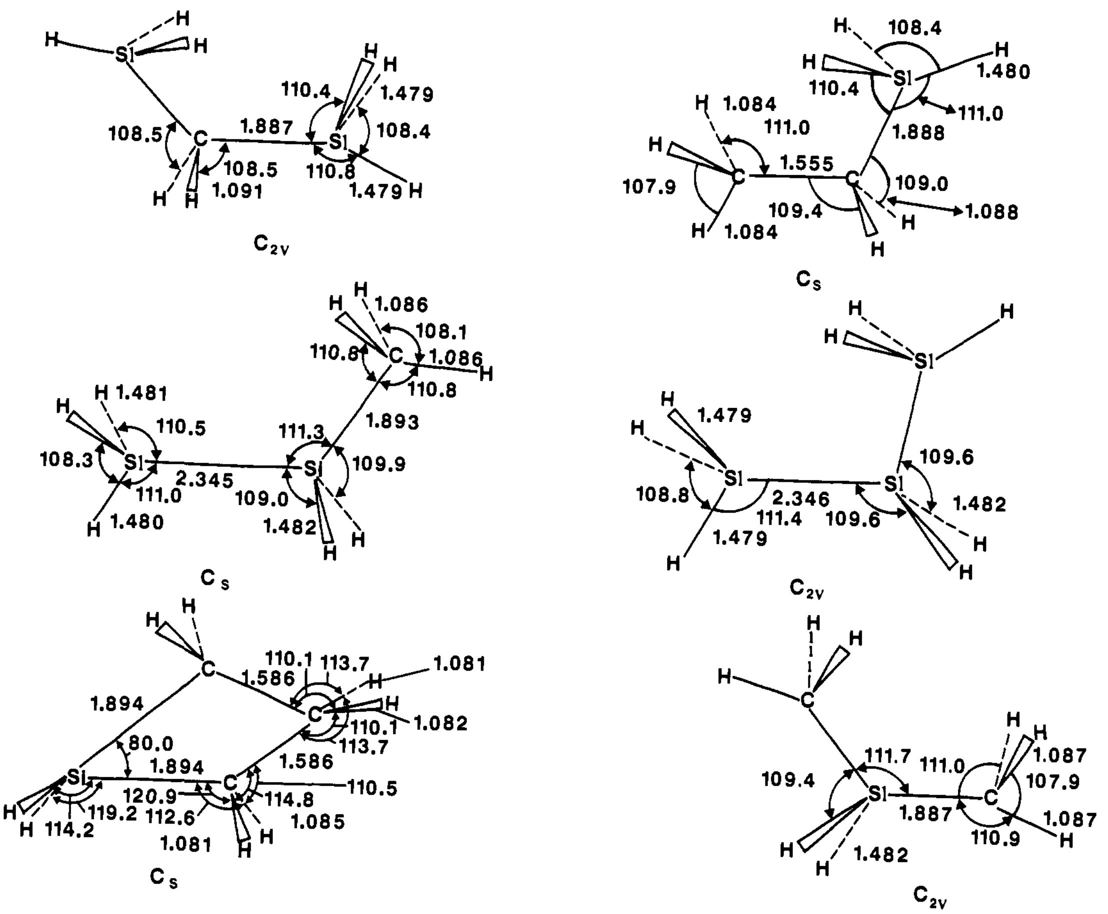

Figure 1. 3-21G* structures for insertion products. Bond lengths are given in Å, angles in deg.

MP3/6-31G(d)//3-21G) obtained at the self-consistent-field (SCF) level. At the MP4/MC-311++G(3df,3pd)[15]//MP2/MC-311G(2D,2P)[15] level, calculations predict that the insertion of silylene into the H-H bond of H_2[6] occurs with an activation energy of less than 2 kcal/mol, after correcting for zero-point vibrational energies (ZPE). This is in good agreement with the most recent experiments,[16] which predict an activation energy of 1 kcal/mol. Furthermore, an interesting feature of the ab initio potential energy surface (PES) is that a shallow well separates the reacting fragments from the transition state.[6] Several experimental groups are attempting to detect this apparent van der Waals minimum.[17]

In earlier calculations from this laboratory zero barriers were reported[9c] for the insertion of CH_2 into the X-H bonds of methane and silane and for SiH_2 into SiH_4 at the MP3/6-31G(d)//3-21G level of theory. For the SiH_2 insertion into a C-H bond of methane, the predicted activation energy[9c] of 22 kcal/mol (at the same level of theory) may be compared with the experimental estimate of 17-19 kcal/mol.[18]

Studies on larger molecules are less common. Insertions into X-Y bonds, where X and Y are both heavy atoms, are observed to occur more slowly than those into X-H or Y-H bonds,[9e] apparently due to a larger barrier, at least in the case of X-Y = C-C.[9e] On the other hand, the MP3/6-31G(d)//SCF/6-31G(d) barrier for the CH_2 insertion into a strained C-C bond in cyclopropane is nearly zero.[9e]

A theoretical study of the reaction of methylene with ethylene at the MP3/6-31G*//3-21G level of theory has predicted a barrier of essentially zero for the insertion of singlet CH_2 into the C-H bond, while the abstraction of an H by triplet CH_2 was found to have a barrier of 24.4 kcal/mol.[19]

In this paper we present the results of ab initio calculations on the insertion of the lowest singlet ($^1A_1$) states of methylene and silylene into the X-Y bonds of ethane, disilane, methylsilane, and cyclopropane and into the X-H bonds of ethane and disilane, with particular interest in the relative magnitudes of X-Y vs X-H insertion barriers.

II. Computational Methods

Optimized geometries for the stationary points were obtained at the restricted Hartree-Fock (RHF) level, using the 3-21G*[20] basis set and the Schlegel optimization method[21] in GAUSSIAN82.[22] Minima and transition states were verified by establishing that the matrices of energy second derivatives have zero and one negative eigenvalue, respectively. Energy differences for reactions (ΔE) augmented by the difference in vibrational zero-point energy (ZPE) give rise to the reaction enthalpy ΔH. Since vibrational frequencies obtained in this manner are systematically too high, the ZPE are multiplied by a scale factor of 0.89.[23]

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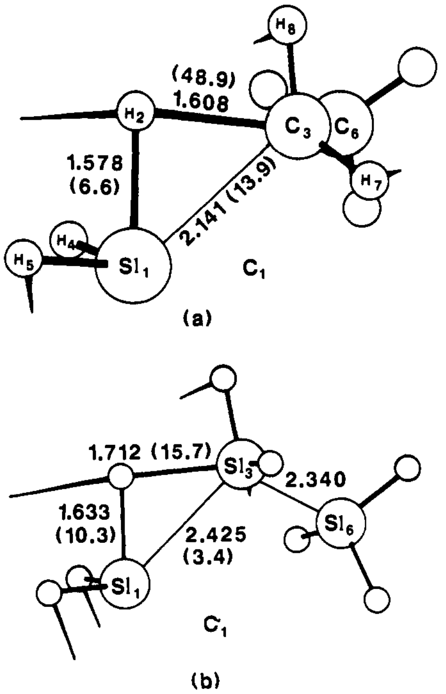

Figure 2. Transition states for the insertions of SiH_2 into (a) C_2H_6 and (b) Si_2H_6. Bond lengths in Å, angles in deg. Arrows illustrate the direction of atoms in the imaginary normal coordinate.

Similarly, the classical barrier height E_b augmented by the scaled ΔZPE yields the activation energy E_a.

The reaction energetics were determined by using second-, third-, and fourth-order Møller–Plesset[24] perturbation theory corrections to the RHF wave functions with the 6-31G(d) basis set. The effect of triple excitations is included for several of the reactions.

The average effect of triple excitations relative to MP4(SDQ) ΔE's can be used to estimate ΔE [MP4(SDTQ)] for the remaining reactions.

III. Results and Discussion

A. Structures. The product equilibrium geometries are displayed in Figure 1. Structures not shown in this figure have been reported previously.[2,3,5,6,9] Figure 2, a and b, illustrates the transition-state geometries for the insertions of SiH_2 into the C–H and Si–H bonds of C_2H_6 and Si_2H_6, respectively. The arrows in the figures illustrate the directions in which the atoms move in the normal coordinate corresponding to the imaginary frequency. Note that at the transition state in Figure 2a the breaking C–H bond is stretched by 49% relative to its equilibrium value, while the Si–H bond in Figure 2b is only 16% longer than its equilibrium value. Thus, the barrier is encountered earlier in the reaction for the Si–H bond than for the C–H bond. As demonstrated below, this is consistent with the Hammond postulate[25] which associates an earlier transition state with a smaller barrier and a more exothermic reaction. The orientation of the attacking SiH_2 is such that the steric repulsions between it and the substrate are minimized. The methyl and silyl groups are bent away from the plane of attack, and the symmetry of these transition states is C_1.

The transition-state geometries for the insertions of silylene into the X–Y bonds of ethane, methylsilane, disilane, and cyclopropane are depicted in Figure 3a–d, respectively. Figure 4, a and b, illustrates the transition states for methylene inserting into the X–Y bonds of methylsilane and disilane, respectively. Note that the complete geometry is given in Table VI for each of the transition states depicted in the figures. The geometries of all structures shown in Figures 3 and 4 are near C_s symmetry, although no symmetry restrictions were imposed in the transition-state searches. In every case the attacking methylene or silylene group orients itself in a manner such that its hydrogen atoms straddle the hydrogens of the more distant member of the X–Y bond at the transition state. The exception to this is the insertion into cyclopropane, for which there are no in-plane hydrogens.

Table I. Relationship between Barrier Heights and Stretching of X–Y Bonds in Transition States

attacking group	E_b for breaking X–Y bond C–C	C–Si	Si–Si	% X–Y bond stretched C–C	C–Si	Si–Si
CH_2	46.0	15.1	0[b]	24[a]	8.8	1.9
SiH_2	61.8	22.3	7.0	40.7	15.3	7.2

[a] Reference 9e. [b] Barriers in kcal/mol calculated at the MP4/6-31G(d)//3-21G* level (CH_2 + C_2H_6 was obtained at the MP4/6-31G(d)//6-31G(d) level of theory).

Examination of the breaking X–Y bonds reveals that those bonds which are longest in their equilibrium structures are stretched by the smallest percentage at the transition state, whether the attacking group is CH_2 or SiH_2 (see Table I). That is, the bond which is stretched the least is the Si–Si bond, and the one stretched the most is the C–C bond. This is indicative of a progressively earlier transition state as the substrate bond increases in length. Note also that CH_2 stretches a given X–Y bond less at the transition state in every case, so that in this sense the CH_2 insertions are earlier than SiH_2 insertions. These observations will be related to the predicted energetics below.

In the SiH_2–cyclopropane transition state the two forming Si–C bonds have unequal lengths. The hydrogens of the incoming silylene are oriented away from those attached to the closer substrate carbon, again in order to minimize steric repulsions. Note that the distance between C_1 and C_3 is about 33% greater than the equilibrium C–C distance in ethane in comparison with 13% when the attacking group is CH_2.[9e] This is consistent with the results presented above and in Table I.

B. Energetics. The total energies for the stable structures and transition states are presented in Tables II and III, respectively. Table IV contains the values used to calculate experimental enthalpies for the reactions. Because of the uncertainty in these values, particularly for the alkylsilanes,[28] these values have been obtained in several ways: (A) These are primarily experimentally measured values. The two exceptions are $CH_3SiH_2SiH_3$ and $(SiH_3)_2CH_2$. Since the enthalpies of formation of these compounds are not known experimentally, they have been estimated by using the homodesmic reactions R1 and R2, respectively.[27] Because

$$CH_3SiH_2SiH_3 + SiH_3CH_3 \rightarrow SiH_3SiH_3 + CH_3SiH_2CH_3 \quad (R1)$$

$$SiH_3CH_2SiH_3 + 2CH_3CH_3 \rightarrow 2SiH_3CH_3 + CH_3CH_2CH_3 \quad (R2)$$

the *relative* alkylsilane heats of formation are expected to be more reliable than the absolute values,[28a] two additional sets of alkylsilane heats of formation have been obtained by using alternative values for methylsilane and then adjusting the remaining alkylsilane heats of formation with reactions R1–R5. In columns

$$SiH_3CH_2CH_3 + CH_3CH_3 \rightarrow SiH_3CH_3 + CH_3CH_2CH_3 \quad (R3)$$

$$CH_3SiH_2CH_3 + 2SiH_3SiH_3 \rightarrow 2SiH_3CH_3 + SiH_3SiH_2SiH_3 \quad (R4)$$

$$c\text{-}[SiC_3H_8] + 4CH_3CH_3 \rightarrow CH_3SiH_2CH_3 + 3CH_3CH_2CH_3 \quad (R5)$$

B and C of Table IV, the (298 K) enthalpy of formation for methylsilane is taken to be −2.0 and −4.8 kcal/mol, respectively. The first of these values will be discussed below. The latter is

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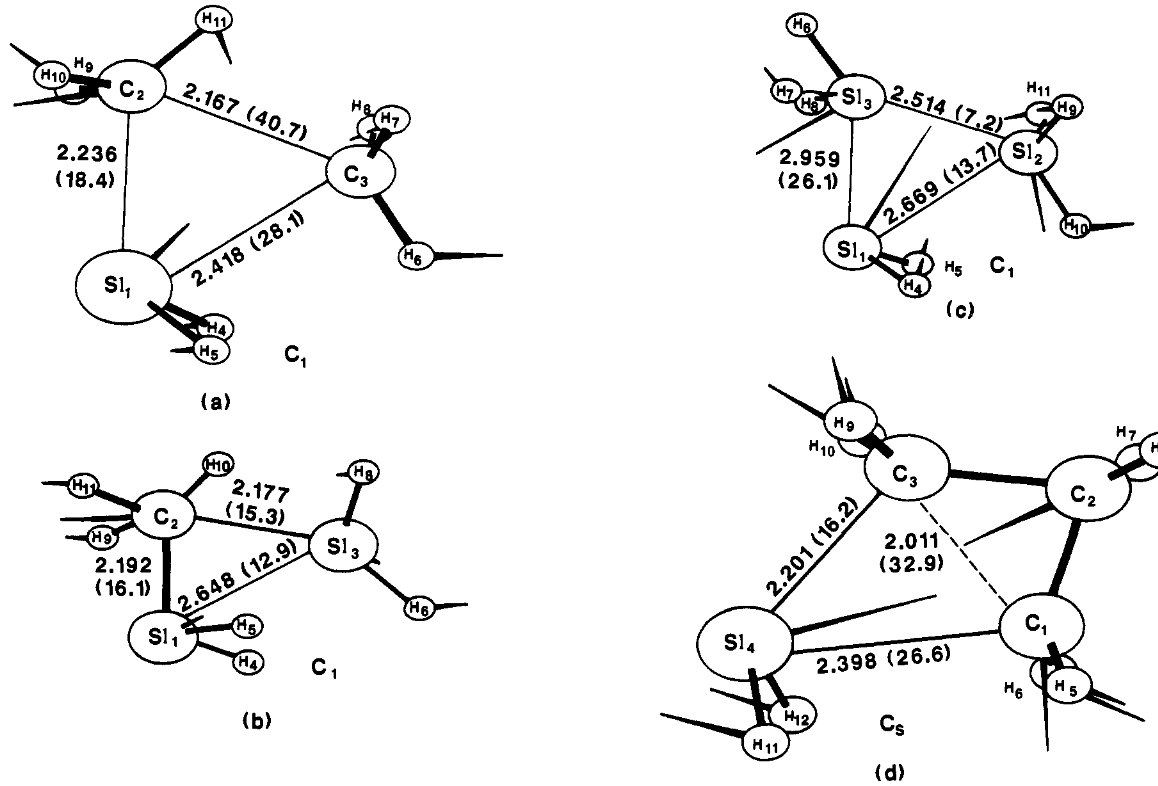

Figure 3. Transition states for the insertion of SiH_2 into the X–Y bond of (a) C_2H_6, (b) CH_3SiH_3, (c) Si_2H_6, and (d) cyclopropane. Bond lengths in Å, angles in deg. Arrows illustrate the direction of motion of atoms in the imaginary normal coordinate.

Table II. 6-31G(d)//3-21G* Total Energies (hartrees) and ZPE (kcal/mol) for Stable Structures

molecule	SCF	MP2	MP3	MP4(SDQ)	MP4(SDTQ)	ZPE
CH_2	−38.87225	−38.96986	−38.98772	−38.99199	−38.99339	11.0
SiH_2	−290.00012	−290.06924	−290.08679	−290.09281	−290.09282	7.9
C_2H_6	−79.22861	−79.49429	−79.52042	−79.52586	−79.53215	50.2
CH_3SiH_3	−330.27134	−330.48512	−330.51367	−330.52014	−330.52495	41.0
Si_2H_6	−581.30476	−581.46685	−581.50016	−581.50801	−581.51137	33.0
C_3H_8	−118.26339	−118.65963	−118.69534	−118.70259		
$CH_3CH_2SiH_3$	−369.30185	−369.64640	−369.68446	−369.69283	−369.70193	60.5
$CH_3SiH_2CH_3$	−369.31800	−369.66326	−369.70173	−369.70989	−369.71846	60.6
$SiH_3SiH_2CH_3$	−620.35017	−620.64406	−620.68699	−620.69653	−620.70375	52.7
Si_3H_8	−871.38615	−871.62908	−871.67654	−871.68725	−871.69309	44.8
c-C_3H_6[a]	−117.05887	−117.44820	−117.47640	−117.48196	−117.49407	54.8
c-C_4H_8	−156.09720	−156.61720	−156.65531	−156.66303	−156.67955	74.5
C_3H_8	−118.26365	−118.65997	−118.69565	−118.70292	−118.71338	69.4
CH_2	−38.87237	−38.96988	−38.98772	−38.99198	−38.99337	11.3
C_2H_6	−79.22876	−79.49451	−79.52062	−79.52606	−79.53234	50.0
c-C_3H_6	−117.05840	−117.44777	−117.47604	−117.48158	−117.49379	54.8
$CH_2(SiH_3)_2$	−620.34975	−620.64257	−620.68285	−620.69213	−620.69978	51.6
c-SiC_3H_8	−407.14721	−407.61866	−407.65916	−407.66785	−407.68308	66.5

[a] 6-31G(d) geometry.

Table III. 6-31G(d)//3-21G* Total Energies (hartrees) and ZPE (kcal/mol) for Transition States

structure	bond	SCF	MP2	MP3	MP4(SDQ)	MP4(SDTQ)	ZPE
SiH_2 + C_2H_6	C–H	−369.14733	−369.51544	−369.55531	−369.56480	−369.57681	58.5
SiH_2 + C_2H_6	C–C	−369.10322	−369.47063	−369.50887	−369.52011		60.1
CH_2 + Si_2H_6	Si–Si	−620.16947	−620.44497	−620.49358	−620.50556		47.4
SiH_2 + $CSiH_6$	C–Si	−620.21514	−620.52483	−620.56721	−620.57743		52.6
CH_2 + $CSiH_6$	C–Si	−369.09374	−369.43769	−369.47772	−369.48813		57.1
SiH_2 + Si_2H_6	Si–Si	−871.27609	−871.52953	−871.57848	−871.58971		44.1
SiH_2 + Si_2H_6	Si–H	−871.29518	−871.54961	−871.59808	−871.60898		43.6
SiH_2 + c-C_3H_6	C–C	−407.00188	−407.49229	−407.53119	−407.54237		64.7
CH_2 + C_2H_6	C–C[a]	−117.99731	−118.39885	−118.43480	−118.44480	−118.45910	66.2
CH_2 + C_2H_6	C–H[a]	−118.07477	−118.47087	−118.50796	−118.51647	−118.52811	65.4
CH_2 + c-C_3H_6	C–C[a]	−155.90035	−156.42456	−156.46066	−156.47024	−156.49046	70.9

[a] Optimized at the 6-31G(d) level.

that predicted by G1 theory[29] and is expected to be within 2 kcal/mol of experiment.

The reaction energetics and activation energies are shown in Table V. The insertions of methylene and silylene into the X–Y bonds of ethane and the insertion of methylene into the X–H bond of ethane and the X–Y bond of cyclopropane have been calculated with and without triple excitations included in the fourth-order

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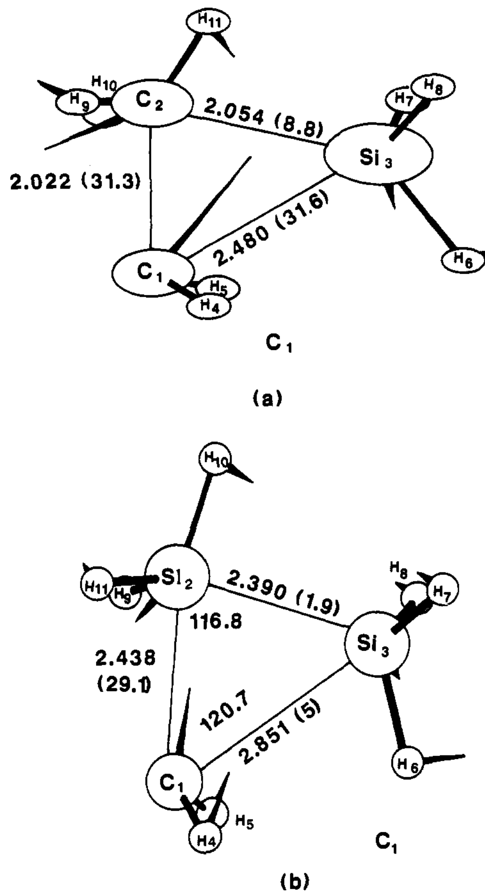

Figure 4. Transition states for the insertions of CH_2 in the X–Y bonds of (a) CH_3SiH_3 and (b) Si_2H_6. Bond lengths in Å, angles in deg. Arrows illustrate the directions of motions of atoms in the imaginary normal coordinate.

Table IV. Experimental Heats of Formation (kcal/mol) for Stationary Point Compounds

	A	B	C
CH_2	101.3[a]		
SiH_2	65.3[b]		
Si_2H_6	19.1[b]		
Si_3H_8	28.9[b]		
C_2H_6	−20.24[c]		
C_3H_8	−24.83[c]		
SiH_3CH_3	−6.96[d]	−2.0	−4.8
$SiH_3CH_2CH_3$	−9.0[d]	−3.7	−6.5
$CH_2(SiH_3)_2$	1.8[e]	11.7	6.1
c-SiC_3H_8	9.3[f]	22.6	17.0
$SiH_2(CH_3)_2$	−22.6[d]		
c-C_3H_6	12.73[c]		
c-C_4H_8	6.8[c]		
$CH_3SiH_2SiH_3$	4.2[e]	9.6	6.8

[a] References 33 and 34. [b] Reference 35. [c] Reference 26. [d] Reference 28a. [e] From homodesmic reaction: see text. [f] Reference 38.

perturbation treatment. The effect of triple excitations is to consistently lower the calculated barrier heights and overall reaction energies by about 4 and 2 kcal/mol, respectively. The full fourth-order perturbation results for the remaining reactions in Table V have been estimated by subtracting these values from the MP4(SDQ) results. Perturbation theory corrections generally have a significant effect on the reaction energetics, both the overall thermodynamics and the calculated barrier heights. Several barriers drop to near zero upon addition of correlation corrections. These include the insertions of CH_2 into the disilane Si–Si bond, the ethane C–H bond, and the cyclopropane C–C bond, as well as the insertion of SiH_2 into the disilane Si–Si bond. As noted above, there is a correlation between the vanishingly small barriers and the early nature of the corresponding transition states.

No transition state could be found for the case of CH_2 inserting in the Si–H bond of Si_2H_6, and we suspect that this reaction occurs with no barrier. This is in agreement with the experimental results[30] of Mazac and Simons that methylene prefers insertion into Si–H over C–H by a factor of 8.9/1. At the MP4/6-31G(d)//6-31G(d) level the barrier for insertion of CH_2 into a C–H bond of C_2H_6 is 0.9 kcal/mol. Thus one would not expect to find a barrier at any level for insertion into a Si–H bond.

If one compares methylene and silylene as they insert into C–C, C–Si, and Si–Si, one sees that in each case there is a progressive increase in E_b as the bond length gets shorter in the substrate. Note that this does not necessarily correlate with the strength of the substrate X–Y bond, since C–Si and C–C bonds have comparable strengths.[31] This suggests that steric factors play an important role in determining the relative barrier heights (see Table I).

There is less than a complete correlation between barrier height and the exothermicity of the reaction. For example, the barrier for the CH_2 insertion into the C–C bond of ethane is much higher than that for CH_2 into the C–Si bond of methylsilane, even though the exothermicities of the two reactions are similar. Of course, the same may be said regarding the CH_2 insertions into the C–H and C–C bonds of ethane. Similarly the most exothermic SiH_2 insertion into an acyclic X–Y bond is that into ethane, and this reaction has the largest calculated barrier.

Now, consider the barriers for methylene and silylene insertion into the strained bonds of cyclopropane. As noted earlier the methylene barrier is 2.3 kcal/mol, about 44 kcal/mol less than that for the analogous insertion into the C–C bond of ethane. This is consistent with the recent observation[32] that singlet methylene inserts into the Si–C, as well as the C–H, bonds of 1,1-dimethylsilacyclobutane. The calculated barrier for the silylene insertion into cyclopropane is about 20 kcal/mol, much larger than that predicted for the corresponding methylene insertion, but about 41 kcal/mol less than that for the silylene insertion into the unstrained C–C bond of ethane. Thus, it is generally much easier to insert into a highly strained C–C bond (in cyclopropane) than into an unstrained one (in ethane).

To assess the quality of the theoretical predictions of the overall reaction enthalpies for the reactions considered here, the three sets of experimental heats of formation discussed above and listed in Table IV have been used to obtained corresponding reaction enthalpies. As noted in previous work,[28b] the CH_2 singlet–triplet splitting is predicted to be 7 kcal/mol too large at the MP4/6-31G(d) level of theory. Thus for those reactions in which (singlet) CH_2 appears as a reactant, the theoretical values of ΔH have been corrected by this amount in Table V.

The first set of experimental values (labeled A in Table V) is taken from the commonly accepted experimental values, plus the homodesmic reactions R1 and R2. To highlight the difficulty with these values, the root-mean-square (RMS) error has been computed only for those reactions in which an alkylsilane is involved. The overall RMS error is smaller than that shown in Table V. Since the RMS error in column A is much larger than expected, the 298 K enthalpy of formation of CH_3SiH_3 was estimated by using reactions R6–R9. The enthalpies of formation predicted

$$SiH_3CH_3 + SiH_2 \rightarrow SiH_3SiH_3 + CH_2 \qquad (R6)$$

$$SiH_3CH_3 + CH_2 \rightarrow CH_3CH_3 + SiH_2 \qquad (R7)$$

$$SiH_3CH_3 \rightarrow SiH_2 + CH_4 \qquad (R8)$$

$$SiH_3CH_3 \rightarrow CH_2 + SiH_4 \qquad (R9)$$

by these four reactions are −5.0, −1.4, −0.1, and −2.1 kcal/mol,

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Table V. Barriers, Reaction Energetics, and Experimental Enthalpies[d]

system	bond	level[e]	E_b	E_a	ΔE	ΔH	ΔH(exptl)[f]		
							A	B	C
$CH_2 + Si_2H_6$	Si–Si	SCF	4.7	6.5	−108.4	−103.2	−118.6	−108.7	−114.3
		MP2	−5.2	−3.4	−129.2	−124.0			
		MP3	−3.6	−1.8	−122.3	−117.1			
		MP4	−3.5	−1.7	−120.6	−115.4			
		MP4[a]	−7.4	−5.6	−122.4	−117.2			
						−110.2[h]			
$CH_2 + CH_3SiH_3$	C–Si	SCF	31.3	34.2	−99.3	−97.8	−103.3	−103.0	−103.0
		MP2	10.8	13.8	−120.1	−118.6			
		MP3	14.8	17.8	−114.9	−113.4			
		MP4	15.1	18.0	−113.4	−111.9			
		MP4[a]	11.2	14.1	−115.2	−113.7			
						−106.7[h]			
$CH_2 + C_2H_6$	C–C[b]	SCF	65.1	67.9	−102.0	−96.5	−105.7	−105.7	−105.7
		MP2	41.1	43.9	−122.7	−117.2			
		MP3	46.1	48.9	−117.5	−112.0			
		MP4	46.0	48.8	−116.0	−110.5			
		MP4[a]	41.8	44.6	−117.8	−112.3			
						−105.3[h]			
$CH_2 + C_2H_6$	C–H[b]	SCF	16.5	18.6	−102.0	−96.5	−105.7	−105.7	−105.7
		MP2	−4.1	−2.0	−122.7	−117.2			
		MP3	0.2	2.3	−117.5	−112.0			
		MP4	0.9	3.0	−116.0	−110.5			
		MP4[a]	−1.5	0.2	−117.8	−112.3			
						−105.3[h]			
CH_2 + c-C_3H_6	C–C[b]	SCF	19.4	22.4	−104.1	−98.4	−107.2	−107.2	−107.2
		MP2	−4.1	−1.1	−125.0	−119.2			
		MP3	2.2	5.2	−126.3	−114.3			
		MP4	2.3	5.3	−118.6	−112.9			
		MP4[a]	−1.9	0.1	−120.6	−114.9			
						−107.9[h]			
$SiH_2 + Si_2H_6$	Si–Si	SCF	18.1	20.2	−51.0	−48.4	−55.5	−55.5	−55.5
		MP2	4.1	6.2	−58.3	−55.7			
		MP3	5.3	7.4	−56.2	−53.6			
		MP4	7.0	9.1	−54.9	−52.3			
		MP4[c]	3.1	5.2	−55.8	−53.2			
$SiH_2 + CH_3SiH_3$	C–Si	SCF	35.3	37.0	−49.4	−46.9	−54.1	−53.7	−53.7
		MP2	18.5	20.2	−56.3	−53.8			
		MP3	20.9	22.6	−54.3	−51.8			
		MP4	22.3	24.0	−53.1	−50.6			
		MP4[c]	18.4	20.1	−54.0	−51.5			
$SiH_2 + C_2H_6$	C–C	SCF	78.8	79.5	−56.0	−54.8	−67.5	−57.1	−62.7
		MP2	58.3	59.0	−62.6	−61.4			
		MP3	61.7	62.4	−59.3	−58.1			
		MP4	61.8	62.5	−57.9	−56.7			
		MP4[a]	56.9	57.6	−58.7	−57.5			
$SiH_2 + Si_2H_6$	Si–H	SCF	6.1	7.3	−51.0	−48.4	−55.5	−55.5	−55.5
		MP2	−8.5	−7.3	−58.3	−55.7			
		MP3	−7.0	−5.8	−56.2	−53.6			
		MP4	−5.1	−3.9	−54.9	−52.3			
		MP4[c]	−9.0	−7.8	−55.8	−53.2			
$SiH_2 + C_2H_6$	C–H	SCF	51.1	50.3	−45.9	−45.0	−53.9	−48.6	−51.4
		MP2	30.2	29.4	−52.0	−51.1			
		MP3	32.6	31.8	−48.5	−47.6			
		MP4	33.8	33.0	−47.2	−46.3			
		MP4[c]	29.9	29.1	−48.3	−47.4			
SiH_2 + c-C_3H_6	C–C	SCF	35.5	36.6	−55.7	−53.6	−68.7	−55.4	−61.0
		MP2	15.5	16.5	−63.8	−61.7			
		MP3	19.9	20.9	−60.4	−58.3			
		MP4	20.1	21.1	−59.3	−57.2			
		MP4[c]	16.2	17.2	−60.5	−58.4			
RMS error[g]							7.4	1.7	3.2

[a] MP4 (SDTQ). [b] Reference 9e. [c] MP4 (SDTQ) estimated based on the average of the four calculated values. (All ΔE and ΔH values are directly calculated values.) [d] In kcal/mol. All reactions containing Si were optimized with use of 3-21G* basis sets (single points 6-31G(d)). The remaining reactions were optimized at the 6-31G(d) level. [e] "Corrected" values are adjusted for the 7 kcal/mol error in the methylene singlet–triplet splitting at the MP4/6-31G(d) level of theory. [f] A, B, and C refer to the three methods for deducing alkylsilane heats of formation: see text. [g] For alkylsilane reactions only. [h] Corrected.

respectively. All of these values are smaller than the currently accepted value of −6.96 kcal/mol. With use of the average of the four values, −2.0 kcal/mol, the heats of formation for the remaining alkylsilanes have been reevaluated by using reactions R1–R5, and these have in turn been used to determine the experimental reaction enthalpies labeled B in Table V.

While the theoretical reaction enthalpies are in much better agreement with the experimental values in column B (RMS error

Table VI. Geometric Parameters for Transition States

bond length		bond angle		dihedral angle[a]		bond length		bond angle		dihedral angle[a]	
Insertion of SiH_2 into the C_2H_6 C–H Bond (Figure 2a)											
$RSiH_2$	1.578					RH_7C_3	1.078	$\angle H_7C_3Si$	97.5	$\angle H_7C_3SiC_6$	−115.7
$RSiC_3$	2.141	$\angle C_3SiH_2$	48.4			RH_8C_3	1.081	$\angle H_8C_3Si$	122.8	$\angle H_8C_3SiC_6$	127.8
$RSiH_4$	1.486	$\angle H_4SiH_2$	81.8	$\angle H_4SiH_2C_3$	126.8	RH_9C_6	1.083	$\angle H_9C_6C_3$	111.1	$\angle H_9C_6C_3Si$	64.2
$RSiH_5$	1.487	$\angle H_5SiH_2$	80.7	$\angle H_5SiH_2C_3$	−122.7	$RH_{10}C_6$	1.081	$\angle H_{10}C_6C_3$	110.9	$\angle H_{10}C_6H_9$	108.5
RC_6C_3	1.535	$\angle C_6C_3Si$	105.6	$\angle C_6C_3SiH_2$	257.0	$RH_{11}C_6$	1.086	$\angle H_{11}C_6C_3$	109.2	$\angle H_{11}C_6H_9$	108.0
Insertion of SiH_2 into the Si_2H_6 Si–H Bond (Figure 2b)											
$RSiH_2$	1.633					RH_7Si_3	1.473	$\angle H_7Si_3Si$	98.8	$\angle H_7Si_3SiSi_6$	−117.5
$RSiSi_3$	2.426	$\angle Si_3SiH_2$	44.8			RH_8Si_3	1.484	$\angle H_8Si_3Si$	126.7	$\angle H_8Si_3SiSi_6$	123.8
$RSiH_4$	1.483	$\angle H_4SiH_2$	88.6	$\angle H_4SiH_2Si_3$	127.4	RH_9Si_6	1.477	$\angle H_9Si_6Si_3$	108.8	$\angle H_9Si_6Si_3Si$	53.6
$RSiH_5$	1.484	$\angle H_5SiH_2$	88.4	$\angle H_5SiH_2Si_3$	−126.2	$RH_{10}Si_6$	1.475	$\angle H_{10}Si_6Si_3$	108.4	$\angle H_{10}Si_6H_9$	109.7
$RSiSi_6$	2.340	$\angle Si_6Si_3Si$	99.7	$\angle Si_6Si_3SiH_2$	228.7	$RH_{11}Si_6$	1.480	$\angle H_{11}Si_6Si_3$	111.3	$\angle H_{11}Si_6H_9$	108.9
Insertion of SiH_2 into the C_2H_6 C–C Bond (Figure 3a)											
$RSiC_2$	2.236					RH_7C_3	1.074	$\angle H_7C_3C_2$	88.0	$\angle H_7C_3C_2Si$	123.0
RC_2C_3	2.167	$\angle C_3C_2Si$	66.6			RH_8C_3	1.074	$\angle H_8C_3C_2$	88.0	$\angle H_8C_3C_2Si$	−123.1
RH_4Si	1.496	$\angle H_4SiC_2$	110.2	$\angle H_4SiC_2C_3$	56.3	RH_9C_2	1.077	$\angle H_9C_2C_3$	122.1	$\angle H_9C_2C_3Si$	76.8
RH_5Si	1.496	$\angle H_5SiC_2$	110.2	$\angle H_5SiC_2C_3$	−56.3	$RH_{10}C_2$	1.077	$\angle H_{10}C_2C_3$	122.1	$\angle H_{10}C_2H_9$	111.1
RH_6C_3	1.071	$\angle H_6C_3C_2$	141.9	$\angle H_6C_3C_2Si$	−0.0	$RH_{11}C_2$	1.074	$\angle H_{11}C_2C_3$	74.0	$\angle H_{11}C_2H_9$	109.4
Insertion of SiH_2 into the CH_3SiH_3 C–Si Bond (Figure 3b)											
$RSiC_2$	2.192					RH_7Si_3	1.473	$\angle H_7Si_3Si$	117.3	$\angle H_7Si_3SiH_6$	−110.7
$RSiSi_3$	2.648	$\angle Si_3SiC_2$	52.4			RH_8Si_3	1.473	$\angle H_8Si_3Si$	117.3	$\angle H_8Si_3SiH_6$	110.7
RH_4Si	1.519	$\angle H_4SiC_2$	94.0	$\angle H_4SiC_2Si_3$	−47.5	RH_9C_2	1.083	$\angle H_9C_2Si_3$	124.4	$\angle H_9C_2Si_3Si$	82.3
RH_5Si	1.519	$\angle H_5SiC_2$	94.0	$\angle H_5SiC_2Si_3$	47.6	$RH_{10}C_2$	1.090	$\angle H_{10}C_2Si_3$	75.4	$\angle H_{10}C_2H_9$	104.4
RH_6Si_3	1.471	$\angle H_6Si_3Si$	94.4	$\angle H_6Si_3Si$	180.0	$RH_{11}C_2$	1.083	$\angle H_{11}C_2Si_3$	124.3	$\angle H_{11}C_2H_9$	109.8
Insertion of SiH_2 into the Si_2H_6 Si–Si Bond (Figure 3c)											
$RSiSi_2$	2.669					RH_7Si_3	1.474	$\angle H_7Si_3Si$	120.8	$\angle H_7Si_3H_6$	109.2
$RSiSi_3$	2.959	$\angle Si_3SiSi_2$	52.8			RH_8Si_3	1.474	$\angle H_8Si_3Si$	120.8	$\angle H_8Si_3H_6$	109.2
RH_4Si	1.501	$\angle H_4SiSi_2$	107.5	$\angle H_4SiSi_3$	73.4	RH_9Si_2	1.470	$\angle H_9Si_2Si$	90.0	$\angle H_9Si_2SiSi_3$	122.5
RH_5Si	1.501	$\angle H_5SiSi_2$	107.5	$\angle H_5SiSi_3$	73.4	$RH_{10}Si_2$	1.488	$\angle H_{10}Si_2Si$	148.9	$\angle H_{10}Si_2H_9$	106.1
RH_6Si_3	1.465	$\angle H_6Si_3Si$	79.9	$\angle H_6Si_3SiSi_2$	180.0	$RH_{11}Si_2$	1.470	$\angle H_{11}Si_2Si$	90.0	$\angle H_{11}Si_2H_9$	114.9
Insertion of SiH_2 into the c-C_3H_6 C–C Bond (Figure 3d)											
RCC_2	1.499					RH_8C_2	1.077	$\angle H_8C_2C$	115.0	$\angle H_8C_2C_3$	114.8
RC_3C_2	1.509	$\angle C_3C_2C$	83.5			RH_9C_3	1.073	$\angle H_9C_3C$	122.7	$\angle H_9C_3C_2$	115.3
RSi_4C	2.398	$\angle Si_4CC_3$	59.2	$\angle Si_4CC_3C_2$	180.0	$RH_{10}C_3$	1.073	$\angle H_{10}C_3C$	122.7	$\angle H_{10}C_3C_2$	115.3
RH_5C	1.069	$\angle H_5CC_2$	117.3	$\angle H_5CC_3$	120.0	$RH_{11}Si_4$	1.491	$\angle H_{11}Si_4C$	80.4	$\angle H_{11}Si_4C_3$	111.2
RH_6C	1.069	$\angle H_6CC_2$	117.3	$\angle H_6CC_3$	120.0	$RH_{12}Si_4$	1.491	$\angle H_{12}Si_4C$	80.4	$\angle H_{12}Si_4C_3$	111.2
RH_7C_2	1.077	$\angle H_7C_2C$	115.0	$\angle H_7C_2C_3$	114.8						
Insertion of CH_2 into the CH_3SiH_3 C–Si Bond (Figure 4a)											
RCC_2	2.022					RH_7Si_3	1.475	$\angle H_7Si_3C_2$	97.1	$\angle H_7Si_3C_2C$	−123.5
RSi_3C_2	2.054	$\angle Si_3C_2C$	74.9			RH_8Si_3	1.475	$\angle H_8Si_3C_2$	97.1	$\angle H_8Si_3C_2C$	123.5
RH_4C	1.096	$\angle H_4CC_2$	104.1	$\angle H_4CC_2Si_3$	−57.9	RH_9C_2	1.076	$\angle H_9C_2C_3$	123.1	$\angle H_9C_2C_3C$	78.9
RH_5C	1.096	$\angle H_5CC_2$	104.1	$\angle H_5CC_2Si_3$	57.9	$RH_{10}C_2$	1.076	$\angle H_{10}C_2C_3$	123.1	$\angle H_{10}C_2C_3C$	−78.9
RH_6Si_3	1.475	$\angle H_6Si_3C_2$	137.9	$\angle H_6Si_3C_2C$	0.0	$RH_{11}C_2$	1.100	$\angle H_{11}C_2C_3$	78.6	$\angle H_{11}C_2C_3C$	180.0
Insertion of CH_2 into the Si_2H_6 Si–Si Bond (Figure 4b)											
$RCSi_2$	2.438					RH_7Si_3	1.478	$\angle H_7Si_3Si_2$	107.3	$\angle H_7Si_3Si_2C$	120.9
RSi_3Si_2	2.390	$\angle Si_3Si_2C$	72.4			RH_8Si_3	1.478	$\angle H_8Si_3Si_2$	107.3	$\angle H_8Si_3Si_2C$	−120.8
RH_4C	1.093	$\angle H_4CSi_2$	120.7	$\angle H_4CSi_2Si_3$	70.3	RH_9Si_2	1.472	$\angle H_9Si_2Si_3$	116.8	$\angle H_9Si_2Si_3C$	73.8
RH_5C	1.093	$\angle H_5CSi_2$	120.6	$\angle H_5CSi_2Si_3$	−70.4	$RH_{10}Si_2$	1.509	$\angle H_{10}Si_2Si_3$	93.7	$\angle H_{10}Si_2Si_3C$	180.0
RH_6Si_3	1.486	$\angle H_6Si_3Si_2$	118.6	$\angle H_6Si_3Si_2C$	0.0	$RH_{11}Si_2$	1.472	$\angle H_{11}Si_2Si_3$	116.8	$\angle H_{11}Si_2Si_3C$	−73.8

[a] If only three centers are specified, the angle is a bond angle.

= 1.7 kcal/mol), the reactions used to deduce the adjusted heats of formation, reactions R6–R9, are not homodesmic. Even so, these results strongly suggest that the experimental values need to be adjusted. To investigate this at a much higher level of theory, the methylsilane heat of formation was estimated by the G1 theory recently proposed by Pople and co-workers.[29] This value of −4.8 kcal/mol leads to the enthalpies of formation and reaction enthalpies listed under column C in Tables IV and V, respectively. Again the RMS error in Table V (3.2 kcal/mol) is much better when adjusted values are used.

Since the reactions considered in the present work involve the making and breaking of bonds, it is useful to assess the reliability of the single configuration (RHF)-based methods used in the present work. Two approaches to this assessment have been taken here. First, the stability of an RHF wave function to the relaxation of both spin and symmetry constraints can be determined by evaluating the curvature of the wave function with respect to the corresponding parameters. This is easily done with the GAUSSIAN program,[22] and instability with respect to spin restrictions (that is, to relaxation from RHF to UHF wave functions) is an indication that some amount of multiconfigurational description is necessary. Of the 11 transition states considered here, five are found to be UHF-unstable in this manner. The first three of these are methylene insertions into the heavy atom–heavy atom bonds of ethane, methylsilane, and disilane. To assess the effect of including a multiconfigurational description of the wave functions for these transition states, the program GAMESS[36] was used to perform either generalized valence bond (GVB)[37] or, for those

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cases where GVB was non-convergent (disilane), (2,2) MCSCF calculations. Both GVB and MCSCF wave functions correlated the highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals, since these are the ones that are implicated by the stability check. The GVB perfect pairing approximation includes two configurations, in which HOMO and LUMO, respectively, are doubly occupied. The MCSCF wave function includes the additional configuration in which HOMO and LUMO are each singly occupied.

The importance of configurational mixing is best evaluated by examining the natural orbital occupation numbers n for the "active" orbitals (HOMO, LUMO). For the three transition states mentioned above, n(HOMO) = 1.93, 1.98, 1.94, respectively, while n(LUMO) = 0.07, 0.02, 0.06.

The remaining two transition states, which are found to be UHF-unstable, are those for the insertions of silylene into ethane and cyclopropane. The GVB calculation on the former transition state yields n(HOMO) = 1.87 and n(LUMO) = 0.13. The MCSCF calculation on the latter reaction gives n(HOMO) = 1.83 and n(LUMO) = 0.17. While the amount of mixing for these reactions is somewhat larger than that for those discussed in the previous paragraph, none of these results suggest enough configurational mixing to be seriously concerned about the MP4 *relative* energies discussed in this paper, particularly with regard to the qualitative conclusions drawn here (see following section).

IV. Conclusions

The transition states and associated energy barriers for the insertion of methylene and silylene into the X–Y bonds of methylsilane and disilane have been determined, as well as the barrier for the insertion of silylene into the C–C bonds of cyclopropane and ethane. The insertion of silylene into the X–H bonds of disilane and ethane was studied at the same level of theory. These results suggest that, as expected, insertions into unstrained X–Y bonds generally occur with larger barriers than the corresponding insertions into X–H bonds.

The barriers and activation energies appear to correlate more with the length of the substrate bond than with the net reaction exothermicity; thus, steric interactions appear to be a major factor in determining barrier heights. In agreement with the Hammond postulate,[25] the transition state occurs early in cases where the barrier is low.

It appears that the insertions of methylene into both bonds of disilane occur with no barrier, while the insertion of this species into the X–Y bonds of methylsilane and ethane becomes successively more difficult. The insertion of silylene into the Si–H bond of disilane occurs with virtually no barrier, while the insertion into the Si–Si bond of the same molecule is predicted to have a small, nonzero barrier. The latter is small enough that it may disappear at higher levels of theory. The barrier for silylene insertion into the X–Y bonds of methylsilane and ethane again becomes successively larger. The largest calculated barriers are those for the insertions of methylene and silylene into the C–C bond of ethane. When strain is introduced into this bond, as in cyclopropane, these C–C insertions are each reduced on the order of 40 kcal/mol.

The errors expected in the calculations presented here can be estimated by referring to earlier papers in this series. For example, the activation energy predicted for the insertion of silylene into H_2 at the MP2/6-31G(d) level of theory is 11.0 kcal/mol,[9c] whereas the best calculated value[6] is close to zero, in agreement with experiment. The inclusion of MP4 corrections improves the prediction of activation energies somewhat (up to 2 kcal/mol, according to the Table V). So, in spite of the apparent closer agreement of the insertion of silylene into the C–H bond of methane (as noted in the Introduction), errors in calculated barriers can be fairly large (up to 10 kcal/mol) at the level of theory used here. Nonetheless, the major conclusion—that insertions into unstrained heavy atom–heavy atom bonds requires substantially more energy than do insertions into bonds to hydrogen—will not be affected by such estimated errors. As noted in the discussion given earlier in this paper, the errors in overall energy differences are expected to be rather smaller than those in activation energies.

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