Ab initio study of some free-radical homolytic substitution reactions at silicon, germanium and tin

Carl H. Schiesser,* Michelle L. Styles and Lisa M. Wild

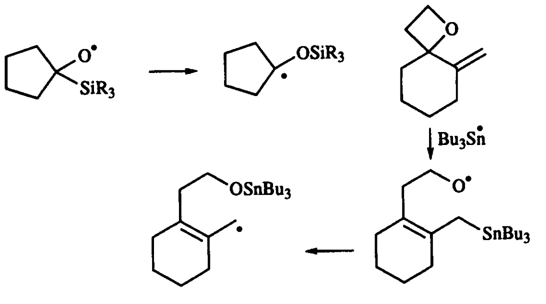
School of Chemistry, The University of Melbourne, Parkville, Victoria, Australia, 3052

***Ab initio* molecular orbital calculations using pseudopotential (DZP) and all-electron (6-311G**) basis sets, with (MP2, QCISD) and without (SCF) the inclusion of electron correlation, predict that hydrogen atoms and methyl radicals undergo homolytic substitution at the heteroatom in silane, germane and stannane without the involvement of hypervalent intermediates. At the QCISD/DZP level of theory, energy barriers of between 69 and 76 kJ mol^{-1} are predicted for attack by a hydrogen atom, while QCISD/DZP//MP2/DZP calculations predict barriers of between 95 and 106 kJ mol^{-1} for attack by a methyl radical, with barriers of 56–69 kJ mol^{-1} for the reverse reactions. When electron correlation is included (MP2), hypervalent intermediates (3) are predicted in reactions involving attack of a methyl radical at methylsilane, methylgermane and methylstannane. QCISD/DZP//MP2/DZP barriers of 86–106 kJ mol^{-1} are predicted for the formation of intermediates (3) which are constrained by barriers of only 2–3 kJ mol^{-1}. When zero-point vibrational energy correction is included, the structures (3) are predicted to behave much more like transition states than intermediates.**

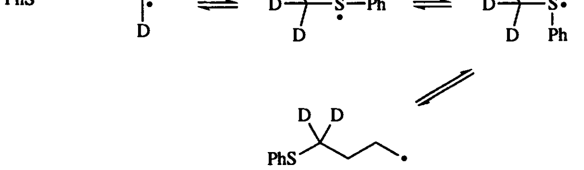
Introduction

Radical rearrangement reactions play important roles in organic chemistry. Intramolecular homolytic addition chemistry is now well regarded as an important tool in synthesis,[1] while homolytic substitution chemistry to effect ring-closure[2] and group transfer processes[3] has found increasing use in the laboratory and is indicative of the direction that free-radical chemistry is headed. Our increased understanding of the factors which govern homolytic substitution reactions through the use of preparative,[2,3] mechanistic and kinetic[4] as well as computational[5] studies has led to the design of 'tailor made' reagents and reactions based on this chemistry.[6]

There are however, several interesting observations which cannot be explained with our current level of understanding.[7] For example, several reports exist in which intramolecular group transfer chemistry has been achieved through free-radical attack at the silicon and tin atoms in alkylsilanes and stannanes.[8–11] Radical Brook-type rearrangements,[8] and the 1,5 and 1,6 transfers of stannyl and silyl groups reported by Kim[9] as well as Davies,[10] are examples of these processes (Scheme 1). In contrast, we are aware of only one example in which a chalcogen is involved in intramolecular homolytic group transfer; we recently demonstrated that the 1,1-dideuterio-4-phenylthio-1-butyl radical rearranges to the isomeric 4,4-dideuterio-4-phenylthio-1-butyl species,†,[12] a reaction most likely to involve a hypervalent [9-S-3] intermediate (Scheme 2). At this time, we are unaware of any examples involving halogen atoms in rearrangements of this type. Why should group IV heteroatoms readily undergo intramolecular homolytic group transfer reactions while there are so few reports for chalcogen- or halogen-containing systems?



Scheme 1



Scheme 2

Work in our group has focussed recently on the design, application and understanding of free-radical homolytic substitution chemistry with the aim of developing novel synthetic methodology. Part of that work has involved the modelling of free-radical attack at higher heteroatoms through the use of *ab initio* molecular orbital techniques. During the course of this work, we reported that homolytic substitution by methyl, silyl, germyl and stannyl radicals at the halogen atom in halomethanes or the chalcogen atom in methanethiol and methaneselenol with expulsion of methyl radical is predicted to proceed readily and without the involvement of hypervalent intermediates.[5i–k] In contrast, the similar substitution reactions at phosphorus and tellurium are often found to involve hypervalent intermediates, especially when electron correlation is included in the calculations.[5h,i,l,m]

In order to provide a better understanding of the mechanistic details of homolytic substitution chemistry at silicon, germanium and tin, we have examined the potential energy surfaces for the attack of the hydrogen atom and methyl radical at the heteroatom in silane (SiH_4), methylsilane ($MeSiH_3$), germane (GeH_4), methylgermane ($MeGeH_3$), stannane (SnH_4) and methylstannane ($MeSnH_3$) with the loss of hydrogen atom or methyl radical. Previous work within the group had demonstrated the (valence) double-ζ pseudopotential basis set of Hay and Wadt (supplemented with a set of polarisation functions)

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† IUPAC names: 4-phenylthio[1,1-$^2H_2$]butyl and 4-phenylthio[4,4-$^2H_2$]butyl, respectively.

to be the basis of choice in calculations involving homolytic substitution at chalcogen.[5m] Specifically, this basis set was the only basis set in an extensive series of all-electron and pseudopotential bases to correctly predict the nature of λ^4-sulfanyl (SH_3), a species with a measured lifetime of at least 0.56 μs.[13] In this work we report the results of calculations involving this basis, as well as (for comparison) the 6-311G** basis set for reactions involving silicon.

Methods

All *ab initio* molecular orbital calculations were carried out using the Gaussian 92[14] or Gaussian 94[15] program. Geometry optimisations were performed using standard gradient techniques at the SCF, MP2 and QCISD (for reactions not involving methyl radicals) levels of theory, using RHF and UHF methods for closed and open shell systems, respectively.[16] Further single-point QCISD calculations were performed on each of the MP2 optimised structures in reactions involving attack of methyl radical. When correlated methods were used calculations were performed using the frozen core approximation.

Whenever geometry optimisations were performed, vibrational frequencies were calculated to determine the nature of located stationary points. Calculations were performed on all reactants, products and transition states to obtain barriers and energies of reaction. Where appropriate, zero-point vibrational energy (ZPE) corrections have been applied.

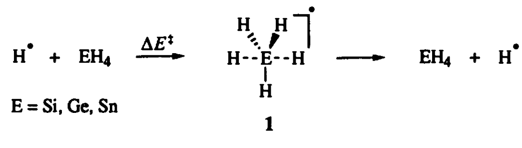
The (valence) double-ζ pseudopotential basis sets of Hay and Wadt[17] supplemented with a single set of d-type polarisation functions were used for the heteroatoms in this study [exponents $d(\zeta)_{Si} = 0.284$,[18] $d(\zeta)_{Ge} = 0.230$[18] and $d(\zeta)_{Sn} = 0.200$] while the double-ζ all-electron basis sets of Dunning[19] with an additional set of polarisation functions [exponents $d(\zeta)_C = 0.75$ and $p(\zeta)_H = 1.00$] were used for C and H. We refer to this basis set as DZP (double-ζ pseudopotential) throughout this work. In addition, the (standard) 6-311G** (triple-ζ) basis set was also used for calculations involving silicon.

Calculations were performed on a Sun Sparcserver 10/512, DEC AlphaStation 400 4/233, Cray Y-MP4E/364 or Cray J916 computer.

Results and discussion

Reaction of hydrogen atoms with silane, germane and stannane (EH_4)

Hypervalent species of D_{3h} symmetry were located on the EH_5 (E = Si, Ge, Sn) potential energy surfaces at all levels of theory and were found to correspond to the symmetrical transition states **1** for the degenerate homolytic substitution reaction of a hydrogen atom at the heteroatom in silane, germane and stannane (Scheme 3). Calculated transition state geometries are displayed in Fig. 1, while the calculated energy barriers ($\Delta E^‡$) for these reactions are listed in Table 1 together with the calculated (imaginary) asymmetric stretching frequency (ν) of each transition state. Calculated energies of all structures in this study are listed in Table 2.



Scheme 3

Table 1 Calculated energy barriers[a] ($\Delta E^‡$) for the homolytic substitution reactions of a hydrogen atom at the heteroatom in silane, germane and stannane (Scheme 3) and asymmetric stretching frequency (ν)[b] of the transition state **1**

1	Method	$\Delta E^‡$	$\Delta E^‡$ (ZPE)	ν
SiH_5	SCF/DZP	127.9	124.9	1504i
	SCF/6-311G**	121.2	117.4	1578i
	MP2/DZP	85.7	86.8	762i
	MP2/6-311G**	79.6	77.5	762i
	QCISD/DZP	71.4	72.0	786i
	QCISD/6-311G**	65.2	62.4	716i
GeH_5	SCF/DZP	129.9	127.4	1517i
	MP2/DZP	92.0	93.3	805i
	QCISD/DZP	76.3	76.9	743i
SnH_5	SCF/DZP	121.6	116.9	1604i
	MP2/DZP	88.5	89.0	839i
	QCISD/DZP	69.3	68.9	674i

[a] Energies in kJ mol^{-1}. [b] Frequencies in cm^{-1}.

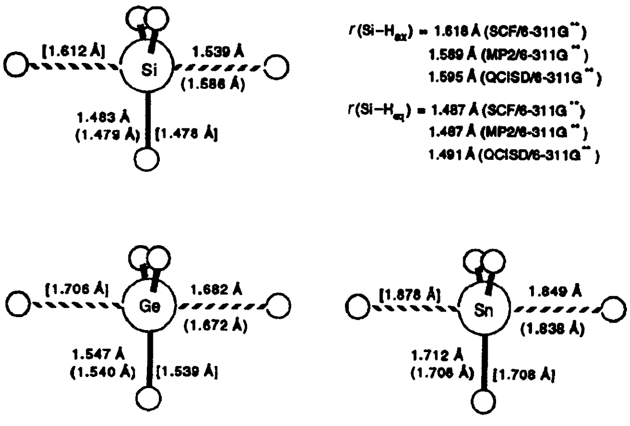


Fig. 1 QCISD/DZP calculated important geometrical features of the transition states **1** involved in the homolytic substitution reactions of a hydrogen atom at the heteroatom in silane (SiH_4), germane (GeH_4) and stannane (SnH_4); (MP2/DZP data in parentheses) [SCF/DZP data in square brackets]. Calculations using the 6-311G** basis set for structures containing silicon are also presented.

Inspection of Table 1 and Fig. 1 reveals a pleasing level of agreement between the results obtained with the DZP basis set and those obtained with the 6-311G** basis for SiH_5. Energy barriers of between 62.3 (QCISD/6-311G** + ZPE) and 127.9 kJ mol^{-1} (SCF/DZP) are predicted for substitution by a hydrogen atom at silane. These are to be compared to a value of 52.9 kJ mol^{-1} (QCISD/DZP) calculated for attack of a hydrogen atom at the sulfur atom in hydrogen sulfide.‡,[14] Inclusion of zero-point energy corrections serve to slightly modify calculated barriers without changing the observed trends.

At the SCF/DZP level of theory silicon–hydrogen separations of 1.478 and 1.612 Å are obtained for the equatorial and axial hydrogens, respectively. These are to be compared with values of 1.487 and 1.618 Å, respectively, at the SCF/6-311G** level. As expected,[5] inclusion of electron correlation serves to reduce the axial Si–H distances, with calculated values of 1.586 (MP2/DZP), 1.589 (MP2/6-311G**), 1.593 (QCISD/DZP) and 1.595 Å (QCISD/6-311G**). Importantly, unlike our previous examination of the H_3S potential energy surface,[5m] both all-electron (6-311G**) and pseudopotential (DZP) basis sets are in good agreement, with similar predictions of the geometry of SiH_5 and its nature (transition state or intermediate) when the same degree of correlation is included. It is clear that at the SCF level, the magnitude of the imaginary frequency is overestimated [1504i (DZP) and 1578i cm^{-1} (6-311G**)]; with the inclusion of electron correlation (MP2, QCISD) we begin to observe convergence in this parameter, with values between 716i and 762i cm^{-1}. These results provide confidence in the ability of the DZP basis set to provide reliable data in homolytic substitution chemistry at silicon, germanium and tin.

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‡ H_3S, H_3Se and H_3Te are predicted to be hypervalent intermediates at the QCISD/DZP level of theory.[14]

Table 2 SCF, MP2 and QCISD calculated energies[a] of the reactants, products, intermediates and transition states (**1–4**) in this study

Structure	SCF/DZP (SCF/6-311G**)	MP2/DZP (MP2/6-311G**)	QCISD/DZP (QCISD/6-311G**)
$^{\cdot}CH_3$	−39.571 76[b] (−39.572 91)	−39.697 27[b] (−39.707 24)	−39.718 91[b,c] (−39.729 13)[d]
SiH_4	−6.090 51 (−291.253 18)	−6.201 71 (−291.371 93)	−6.229 27 −6.229 26[c] (−291.400 86) (−291.400 86)[d]
GeH_4	−5.954 99	−6.063 48	−6.090 69 −6.090 67[c]
SnH_4	−5.539 30	−5.639 52	−5.666 33 −5.666 29[c]
CH_3SiH_3	−45.146 23 (−330.310 30)	−45.398 25 (−330.579 85)	−45.438 18[c] (−330.620 54)[d]
CH_3GeH_3	−45.007 68	−45.257 78	−45.297 15[c]
CH_3SnH_3	−44.591 07	−44.933 87	−44.872 70[c]
SiH_5 (D_{3h}) (**1**)	−6.539 45 (−291.703 24)	−6.666 74 (−291.837 82)	−6.699 75 (−291.872 24)
GeH_5 (D_{3h}) (**1**)	−6.403 17	−6.526 09	−6.559 31
SnH_5 (D_{3h}) (**1**)	−5.990 67	−6.103 48	−6.137 59
CH_3SiH_4 (C_{3v}) (**2**)	−45.594 67 (−330.759 02)	−45.860 53 (−331.041 70)	−45.909 61[c] (−331.092 23)[d]
CH_3GeH_4 (C_{3v}) (**2**)	−45.458 69	−45.720 01	−45.769 01[c]
CH_3SnH_4 (C_{3v}) (**2**)	−45.047 80	−45.298 50	−45.348 92[c]
Me_2SiH_3 (D_{3h}) (**3**)	−84.648 45 (−369.813 12)	−85.056 41 (−370.248 85)	−85.115 86[c] (−370.308 33)[d]
Me_2GeH_3 (D_{3h}) (**3**)	−84.513 46	−84.915 89	−84.975 88[c]
Me_2SnH_3 (D_{3h}) (**3**)	−84.104 74	−84.497 07	−84.557 78[c]
Me_2SiH_3 (C_{3v}) (**4**)	—	−85.055 44 (−370.247 36)	−85.116 95[c] (−370.309 52)[d]
Me_2GeH_3 (C_{3v}) (**4**)	—	−84.915 40	−84.976 68[c]
Me_2SnH_3 (C_{3v}) (**4**)	—	−84.496 11	−84.558 54[c]

[a] Energies in hartrees (1 E_h = 2626 kJ mol^{-1}). [b] These values were previously reported incorrectly (refs. 5*i,j,k*). [c] QCISD/DZP//MP2/DZP. [d] QCISD/6-311G**//MP2/6-311G**.

Somewhat surprisingly, calculations at all levels of theory predict a slight increase in the energy barrier associated with the attack of hydrogen atom at the germanium atom in germane. At the QCISD/DZP + ZPE level, $\Delta E^{\ddagger}$ for this reaction is predicted to be 76.9 kJ mol^{-1}, some 4.9 kJ mol^{-1} higher than that for the same reaction at silicon at the same level of theory and some 8.0 kJ mol^{-1} higher than the QCISD/DZP + ZPE value associated with the attack of a hydrogen atom at stannane (68.9 kJ mol^{-1}).

These data are to be compared with the QCISD/DZP calculated values of 41.3 and 14.2 kJ mol^{-1} for attack of a hydrogen atom at the selenium and tellurium atoms in hydrogen selenide‡ and telluride,‡ respectively.[5m] It would appear that homolytic substitution at chalcogen is predicted to be substantially more facile than the corresponding process at the same-row group IV element.

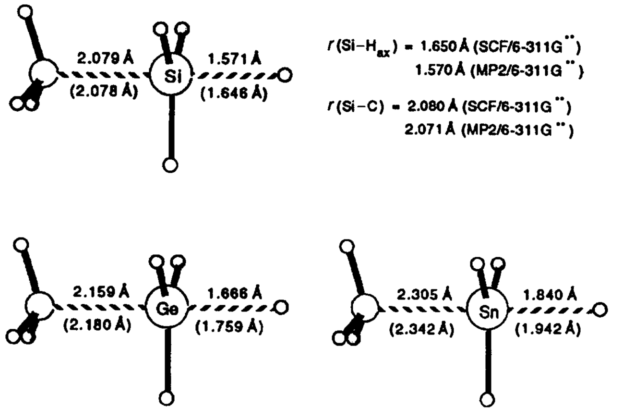
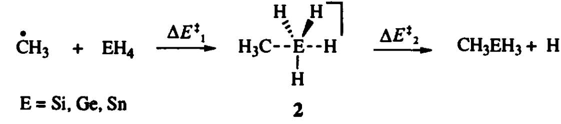


Fig. 2 MP2/DZP calculated important geometrical features of the transition states **2** involved in the homolytic substitution reactions of a methyl radical at the heteroatom in silane (SiH_4), germane (GeH_4) and stannane (SnH_4); (SCF/DZP data in parentheses). Calculations using the 6-311G** basis set for structures containing silicon are also presented.

Reactions of methyl radicals with silane, germane and stannane (EH_4)

Hypervalent species of C_{3v} symmetry were located on the CH_3EH_4 (E = Si, Ge, Sn) potential energy surfaces at all levels of theory and were found to correspond to the transition states **2** for the homolytic substitution reaction of a methyl radical at the heteroatom in silane, germane and stannane with expulsion of a hydrogen atom (Scheme 4). Calculated transition state geometries are displayed in Fig. 2, while the calculated energy barriers for the forward ($\Delta E^{\ddagger}_1$) and reverse ($\Delta E^{\ddagger}_2$) reactions are listed in Table 3 together with the calculated (imaginary) asymmetric stretching frequency (ν) of each transition state. Calculated energies of all structures in this study are listed in Table 2.



Scheme 4

As was previously reported for structures **1**, a pleasing level of agreement between both basis sets in calculated geometry, relative energy and asymmetric stretching frequency for $MeSiH_4$ is observed when the same degree of correlation is included in each calculation. For example, at the MP2 level, values of 2.079 and 1.571 Å for the axial Si–C and Si–H separations are predicted using the DZP basis for $MeSiH_4$, while MP2/6-311G** calculations suggest values for these parameters of 2.071 and 1.570 Å, respectively. As expected, these distances are predicted to increase in the germanium and tin containing transition states **2**; MP2/DZP values of 2.159 (Ge–C), 1.666 (Ge–H_{ax}), 2.305 (Sn–C) and 1.840 Å (Sn–H_{ax}) are obtained.

Table 3 Calculated energy barriers[a] for the forward ($\Delta E^{\ddagger}_1$) and reverse ($\Delta E^{\ddagger}_2$) homolytic substitution reactions of a methyl radical at the heteroatom in silane, germane and stannane (Scheme 4) and asymmetric stretching frequency (ν)[b] of the transition state **2**

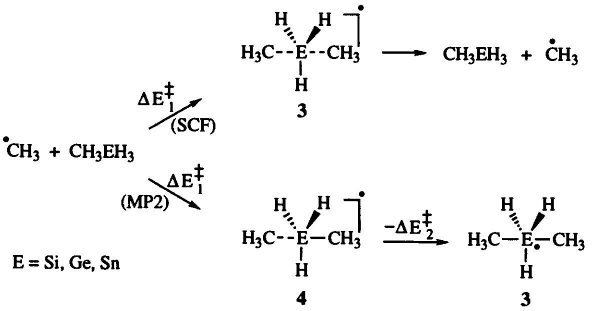
Transition state **2**	Method	$\Delta E^{\ddagger}_1$	$\Delta E^{\ddagger}_1$ + ZPE	$\Delta E^{\ddagger}_2$	$\Delta E^{\ddagger}_2$ + ZPE	ν
$MeSiH_4$	SCF/DZP	177.6	182.8	129.3	132.6	1669i
	SCF/6-311G**	176.2	180.9	124.8	127.9	1795i
	MP2/DZP	101.0	107.3	92.9	99.1	1115i
	MP2/6-311G**	98.4	102.6	90.2	94.9	1224i
	QCISD/DZP[c]	101.3	—	68.9	—	—
	QCISD/6-311G**[d]	99.2	—	64.4	—	—
$MeGeH_4$	SCF/DZP	178.8	183.6	122.5	125.6	1588i
	MP2/DZP	107.0	112.9	93.0	98.9	1084i
	QCISD/DZP[c]	106.6	—	67.7	—	—
$MeSnH_4$	SCF/DZP	166.2	170.0	107.5	109.3	1776i
	MP2/DZP	100.6	104.9	86.7	90.9	1364i
	QCISD/DZP[c]	95.3	—	56.3	—	—

[a] Energies in kJ mol^{-1}. [b] Frequencies in cm^{-1}. [c] QCISD/DZP//MP2/DZP. [d] QCISD/6-311G**//MP2/6-311G**.

As was predicted for the reactions of a hydrogen atom with EH_4, the energy barrier ($\Delta E^{\ddagger}_1$) for the attack of a methyl radical at these species with expulsion of a hydrogen atom is predicted to increase slightly in moving from SiH_4 to GeH_4; MP2/DZP + ZPE calculations predict values of 107.3 and 112.9 kJ mol^{-1} for these reactions, respectively. At the same level, the reaction involving stannane (SnH_4) is predicted to have a slightly lower barrier at 104.9 kJ mol^{-1}. The reverse reactions are predicted to have barriers ($\Delta E^{\ddagger}_2$) of 99.1 (Si), 98.9 (Ge) and 90.9 (Sn) kJ mol^{-1} at MP2/DZP + ZPE level. As expected from previous observations at other heteroatoms,[5] the hydrogen atom is predicted to be the better attacking radical, while the methyl radical is the better leaving group. These data are to be compared with data for the similar attack of a methyl radical at the chalcogen atom in hydrogen sulfide, selenide and telluride. MP2/6-31G** calculations predict a barrier of 95.8 kJ mol^{-1} for the attack of a methyl radical at hydrogen sulfide, with a barrier of 52.7 kJ mol^{-1} for the reverse reaction.[5f] Similarly, MP2/HUZ-SV**//HF/HUZ-SV** calculations predict barriers of 76.6 and 41.4 kJ mol^{-1} for the analogous forward and reverse reactions at the selenium atom in hydrogen selenide.[5e] Clearly, homolytic substitution by a methyl radical at group IV heteroatoms is predicted to be significantly less favourable than for the corresponding process at the same-row chalcogen.

The QCISD/DZP//MP2/DZP calculated energy barriers for the reactions depicted in Scheme 4 show an unexpectedly large deviation from the MP2 calculated data, greater than that observed in the (fully-optimised) QCISD/DZP data for attack of a hydrogen atom at EH_4 and certainly greater than that observed in other calculations performed in our laboratories for homolytic substitution at many other heteroatoms.[5] We suggest that these data be treated with some caution; perhaps the hypervalent structures in these reactions need to be fully optimised at the QCISD level in order to account for small but significant differences in the potential energy surface at the higher level of theory. Similar conclusions were drawn from data pertaining to QCISD/DZP//MP2/DZP calculations on hypervalent Me_2TeH structures.[5h]

Reaction of a methyl radical with methylsilane, methylgermane and methylstannane ($MeEH_3$)



Scheme 5

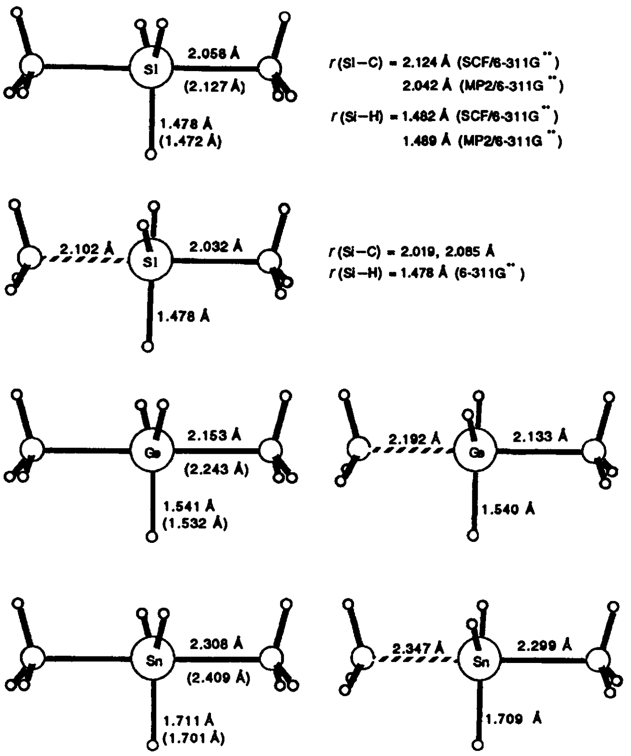


Fig. 3 MP2/DZP calculated important geometrical features of the structures **3** and **4** involved in the homolytic substitution reactions of a methyl radical at the heteroatom in methylsilane ($MeSiH_3$), methylgermane ($MeGeH_3$) and methylstannane ($MeSnH_3$); (SCF/DZP data in parentheses). Calculations using the 6-311G** basis set for structures containing silicon are also presented.

Hypervalent species of D_{3h} symmetry were located on the CH_3EH_4 (E = Si, Ge, Sn) potential energy surfaces at all levels of theory. In SCF calculations, these structures were found to correspond to transition states **3** involved in the degenerate homolytic substitution reaction of a methyl radical at the heteroatom in methylsilane, methylgermane and methylstannane (Scheme 5). When electron correlation is included, structures **3** were found to correspond to hypervalent intermediates. At the MP2 level, transition states **4** for the formation of the intermediates **3** were located and proved to be of C_{3v} symmetry. Calculated geometries of the structures **3** and **4** are displayed in Fig. 3, while the calculated energy differences between **3** and reactants ($Me^{\bullet}$ + $MeEH_3$) ($\Delta E^{\ddagger}_1$) and for the dissociation of the intermediate **4** ($\Delta E^{\ddagger}_2$) at correlated levels of theory are listed in Table 4 together with the calculated asymmetric stretching fre-

Table 4 Calculated energy barriers[a] for the formation ($\Delta E^{\ddagger}_1$) and dissociation ($\Delta E^{\ddagger}_2$) of hypervalent structures **5** involved in the homolytic substitution reactions of a methyl radical at the heteroatom in methylsilane, methylgermane and methylstannane (Scheme 5) and asymmetric stretching frequency (ν)[b] of structures **3** and **4**

						ν	
3, **4**	Method	$\Delta E^{\ddagger}_1$	$\Delta E^{\ddagger}_1$ + ZPE	$\Delta E^{\ddagger}_2$	$\Delta E^{\ddagger}_2$ + ZPE	**3**	**4**
Me_3SiH_3	SCF/DZP	182.7	193.0	—	—	1932i	—
	SCF/6-311G**	184.2	194.7	—	—	2204i	—
	MP2/DZP	105.3	114.9	2.5	(−8.1)	412	1236i
	MP2/6-311G**	104.4	113.4	3.9	(−10.9)	415	1396i
	QCISD/DZP[c]	105.5	—	2.8	—	—	—
	QCISD/6-311G**[d]	105.5	—	(−3.1)	—	—	—
Me_3GeH_3	SCF/DZP	173.4	182.3	—	—	1685i	—
	MP2/DZP	104.1	113.3	1.3	(−6.7)	382	1035i
	QCISD/DZP[c]	103.5	—	2.1	—	—	—
Me_3SnH_3	SCF/DZP	152.6	160.6	—	—	2083i	—
	MP2/DZP	92.0	99.9	2.5	(−12.5)	362	1391i
	QCISD/DZP[c]	86.9	—	2.0	—	—	—

[a] Energies in kJ mol^{-1}. [b] Frequencies in cm^{-1}. [c] QCISD/DZP//MP2/DZP. [d] QCISD/6-311G**//MP2/6-311G**.

quency (ν) of each hypervalent structure. Calculated energies of all structures in this study are listed in Table 2.

Once again a pleasing degree of agreement between all-electron and pseudopotential calculations is observed for attack at methylsilane. For example, at the SCF level of theory the Si–C separations in the transition state **3** are calculated to be 2.127 (DZP) and 2.124 Å (6-311G**). Energy barriers ($\Delta E^{\ddagger}_1$) of 193.0 and 194.7 kJ mol^{-1} are predicted at SCF/DZP and SCF/6-311G**, respectively, when zero-point energy corrections are applied. When electron correlation is included, **3** is found to be bound by a small energy barrier ($\Delta E^{\ddagger}_2$); barriers to dissociation were calculated to be 2.5 (SCF/DZP), 3.9 (SCF/6-311G**) and 2.8 kJ mol^{-1} (QCISD/DZP//MP2/DZP). At the QCISD/6-311G**//MP2/6-311G** level the structure **4** was found to lie below **3** by some 3.1 kJ mol^{-1}. These data suggest that these hypervalent structures need to be fully optimised at the QCISD level of theory to account for slight differences between the QCISD and MP2 generated potential energy surfaces.

The MP2-calculated geometries of the transition states (**4**) and intermediates (**3**) are strikingly similar for a given heteroatom, consistent with small barriers to dissociation for **3**. MP2/DZP data suggest that the E–C distances in **3** are 2.058 (Si), 2.153 (Ge) and 2.308 Å (Sn). The E–C distances in the transition states (**4**) are only slightly perturbed from these values, at 2.032, 2.102 (Si), 2.133, 2.192 (Ge) and 2.299, 2.347 Å (Sn).

Interestingly, when zero-point vibrational energy correction is included, the MP2-calculated transition state (**4**, E = Si) is also found to lie below the energy of the intermediate (**3**, E = Si) by 8.1 (SCF/DZP) and 10.9 kJ mol^{-1} (SCF/6-311G**). Clearly, at the MP2 level, structures **3** are predicted to behave much more like transition states than intermediates. Similar predictions were made for homolytic substitution reactions at some sulfoxides.[5f]

Reactions at the heteroatom in methylgermane and methylstannane are calculated to proceed in similar fashion to the analogous reaction at methylsilane. At the SCF/DZP level of theory, the structures (**3**, E = Ge, Sn) are once again found to correspond to transition states, lying some 182.3 (Ge) and 160.6 kJ mol^{-1} (Sn) above the energy of the reactants when zero-point correction is included. When electron correlation is included (MP2), the structures (**3**, E = Ge, Sn) are predicted to correspond to intermediates. Barriers to dissociation are calculated to be 1.3 (MP2/DZP) and 2.1 kJ mol^{-1} (QCISD/DZP//MP2/DZP) for attack at methylgermane, and 2.5 (MP2/DZP) and 2.0 kJ mol^{-1} (QCISD/DZP//MP2/DZP) for attack at methylstannane. When zero-point correction (MP2/DZP + ZPE) is included, these barriers, once again, vanish [−6.7 (Ge); −12.5 (Sn)].

Of considerable interest are the calculated energy barriers for homolytic substitution by a methyl radical in these systems. At the QCISD/DZP//MP2/DZP level of theory barriers of 105.5, 103.5 and 86.9 kJ mol^{-1} are predicted for attack at the heteroatom in methylsilane, germane and stannane, respectively. These values are substantially higher than those calculated at the same level of theory for the analogous reaction of a methyl radical with methanethiol (87.4 kJ mol^{-1}), methaneselenol (61.3 kJ mol^{-1}) and methanetellurol (24.3 kJ mol^{-1}).[5i,k]

Conclusions

Ab initio molecular orbital calculations predict that homolytic substitutions by a hydrogen atom or methyl radical at the heteroatom in silane (SiH_4), methylsilane ($MeSiH_3$), germane (GeH_4), methylgermane ($MeGeH_3$), stannane (SnH_4) and methylstannane ($MeSnH_3$) with the expulsion of a hydrogen atom or methyl radical, proceed without the involvement of hypervalent intermediates at the SCF level of theory using either a double-ζ pseudopotential (DZP) basis set or the all-electron 6-311G** basis set for silicon. When electron correlation is included (MP2), attack of a methyl radical at methylsilane, germane and stannane is predicted to proceed *via* a hypervalent intermediate of D_{3h} symmetry. These species are calculated to be bound by small energy barriers (1.3–2.2 kJ mol^{-1}) at the MP2 or QCISD//MP2 levels of theory and become unbound when zero-point energy correction is applied.

At the highest level of correlation (QCISD/DZP or QCISD/DZP//MP2/DZP) energy barriers of between 69 and 107 kJ mol^{-1} are predicted for the reaction in this study. These values are significantly larger than those calculated for the corresponding reactions at the sulfur, selenium and tellurium atoms in the analogous sulfide, selenide or telluride. These results suggest that homolytic substitution by the mechanism investigated in this work is most likely not to be viable for reactions involving silyl, germyl or stannyl group transfers between methyl groups. It is unclear whether or not these results are representative of transfers between carbon-centres in general. In similar calculations at other heteroatoms,[5] the differences in activation energy between methyl and other alkyl radical involvement in homolytic substitution reactions at the same heteroatom would not be expected to be large enough to overcome the significant barriers that are predicted in this work. Perhaps the inclusion of further alkyl groups on the heteroatom itself and more appropriate leaving radicals will serve to sufficiently reduce the activation energies associated with transfers of this type involving group IV heteroatoms.

Finally, the intramolecular transfers involving group IV heteroatoms reported to date involve transfers between heteroatoms such as nitrogen, oxygen and sulfur, or between carbon and these heteroatoms.[8–11] Perhaps the inclusion of attacking and leaving groups which incorporate these atoms would have a significant effect on the reaction profiles associated with homolytic substitution at silicon, germanium and tin.

We are exploring further these intriguing reactions by computational and experimental methods.

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