On the radical Brook and related reactions: an *ab initio* study of some (1,2)-silyl, germyl and stannyl translocations

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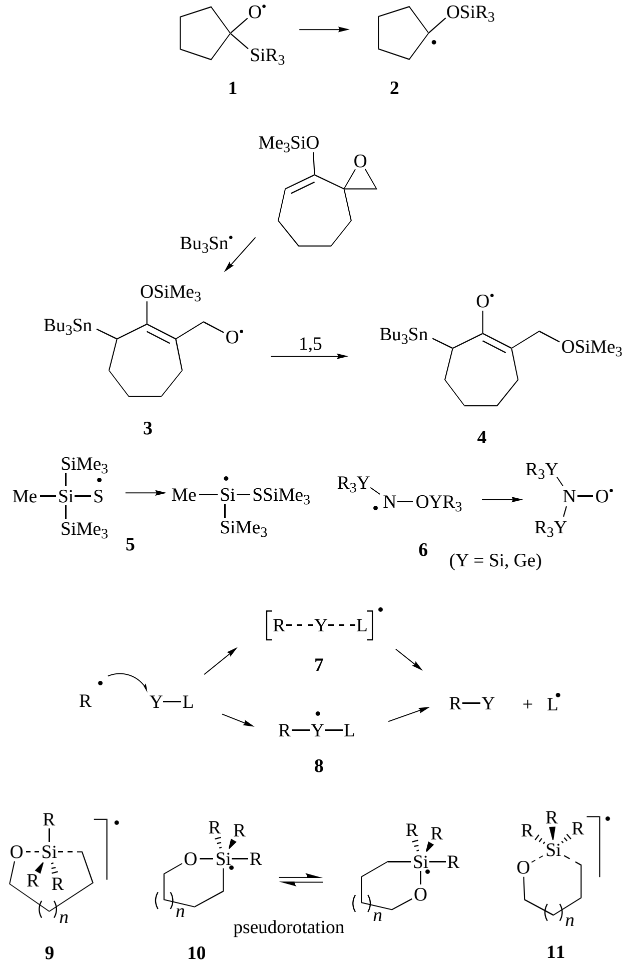
Ab initio **molecular orbital calculations using a (valence) double-ζ pseudopotential basis set (DZP) with (MP2, QCISD) and without (SCF) the inclusion of electron correlation predict that the transition states (12–14) involved in homolytic (1,2)-translocation reactions of silyl (SiH_3), germyl (GeH_3) and stannyl (SnH_3) groups between carbon centres, between carbon and nitrogen, and between carbon and oxygen proceed *via* homolytic substitution mechanisms involving front-side attack at the group (IV) heteroatom. While migrations between carbons are predicted to be unlikely, with calculated activation barriers of 71–137 kJ mol^{-1}, depending on the level of theory, migrations from carbon to nitrogen and from carbon to oxygen are predicted to be facile. For example, rearrangement of the (silylmethyl)aminyl radical ($H_3SiCH_2NH^•$) to the silylaminomethyl species ($H_3SiNHCH_2^•$) is predicted to proceed with a barrier of 50.8–63.2 kJ mol^{-1} when electron correlation is included, in excellent agreement with experimental data. In addition, the analogous translocation to oxygen in the silylmethoxyl radical ($H_3SiCH_2O^•$), the prototypical radical Brook rearrangement, is calculated to require only 19.9 kJ mol^{-1} at the MP2/DZP + ZPVE level. Somewhat unexpectedly, MP2/DZP calculations predict that the stannylmethoxyl radical ($H_3SnCH_2O^•$) rearranges to the stannyloxymethyl radical ($H_3SnOCH_2^•$) without barrier.**

Introduction

Intramolecular (1,*n*) homolytic group transfer chemistry is becoming increasingly popular in free-radical synthesis.[1] Radical Brook-type rearrangements (*e.g.* **1**→**2**),[2] and the 1,5 and 1,6 transfers of stannyl, germyl and silyl groups reported by Kim and co-workers[3,4] (*e.g.* **3**→**4**) as well as Davies and co-workers[5] and others[6] typify the direction that this chemistry is headed (Scheme 1). In addition to the radical Brook rearrangement [(1,2)-translocation of trialkylsilyl from carbon to oxygen], there are several examples of other 1,2 rearrangements involving group (IV) element-containing substituents. Pitt and Fowler reported a radical catalyzed rearrangement in trisilanethiols (*e.g.* **5**),[7] while similar shifts in trialkylsilyl and germyl aminoxyls (**6**) have also been observed.[8–10] Interestingly, we are only aware of one example in which a chalcogen-containing group undergoes intramolecular homolytic translocation,[11] and no examples involving halogen.[1] Why should group (IV) heteroatoms undergo readily intramolecular homolytic group transfer reactions, while there are so few reports for chalcogen or halogen containing systems? The answer to this question almost certainly rests with the intimate details of the homolytic substitution step itself.

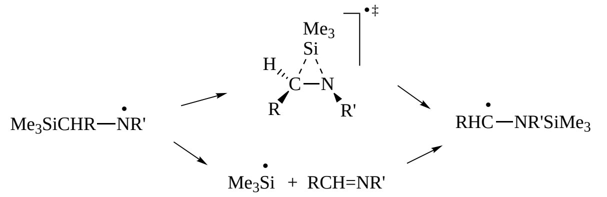
It is generally agreed that homolytic substitution by a radical ($R^•$) at a group (Y) proceeds either *via* a transition state (**7**) in which the attacking and leaving groups adopt a colinear (or nearly so) arrangement resulting in Walden inversion, or with the involvement of a hypervalent intermediate (**8**) which may or may not undergo pseudorotation prior to dissociation.[1] The (1,*n*) translocation of the trialkylsilyl group from carbon to oxygen typifies the intramolecular version of this reaction which might be expected to proceed *via* either transition state (**9**) or intermediate (**10**). If one considers carefully the pathways available for this intramolecular translocation reaction, it seems reasonable that in addition to mechanisms involving structures (**9**, **10**) a third front-side mechanism involving transition state (**11**) is also possible; this mechanism would result in retention of configuration if chiral group (IV)-containing substitutents were involved. Roberts recently suggested that a similar mechanism might be important in hydrogen atom transfers between heteroatoms which have available orbitals and are not coordinately saturated.[12]



Scheme 1

Recently, we reported the results of extensive *ab initio* calculations into the mechanism of intermolecular homolytic substitution by hydrogen atom and methyl radical at the heteroatom in silane, germane, stannane, methylsilane, methylgermane and methylstannane with the expulsion of hydrogen atom or methyl radical.[13] At the QCISD/DZP//MP2/DZP level of theory, calculations predict a Walden inversion mechanism to be unlikely with calculated energy barriers of between 87 and 106 kJ mol^{-1} for the degenerate reactions involving methyl radical. In addition, similar calculations (MP2/DZP) predict a barrier of some 87 kJ mol^{-1} for the degenerate attack of hydroxyl radical at silanol (H_3SiOH) by the Walden inversion mechanism.[14]

Walton, Maillard and co-workers[9] as well as Roberts and Vazquez-Persaud[10] recently examined the rearrangement of some (silylmethyl)aminyl radicals by EPR spectroscopy. While the former study provided estimates of activation energies for these rearrangements (44–58 kJ mol^{-1}), these workers were unable to differentiate between mechanisms involving ‘a transition state in which the silicon atom expands its valence shell to five’[9] or one involving β-elimination followed by recapture of the silyl radical at the nitrogen terminus of the resultant imine (Scheme 2). Roberts and Vazquez-Persaud favoured the concerted mechanism as their study failed to trap trimethylsilyl radicals expected to escape from the solvent cage.[10]



Scheme 2

We now report the results of a high-level *ab initio* investigation into (1,2)-homolytic translocation reactions of silyl, germyl and stannyl groups between carbon centres, between carbon and nitrogen centres and between carbon and oxygen. At the highest level of theory (QCISD/DZP//MP2/DZP), calculations predict energy barriers which include values of 34.2 kJ mol^{-1} for the prototypical radical Brook rearrangement, 63.2 kJ mol^{-1} for the transfer of SiH_3 from carbon to nitrogen in (silylmethyl)aminyl and 103.2 kJ mol^{-1} for the transfer of GeH_3 between carbon centres in 2-(germyl)ethyl and suggest that transfers involving group (IV) element-containing substituents *via* the front-side mechanism may be preferred over the back-side (Walden inversion) mechanism.

Methods

All *ab initio* molecular orbital calculations were carried out using the Gaussian 94 program.[15] Geometry optimisations were performed using standard gradient techniques at the SCF and MP2 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. 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.

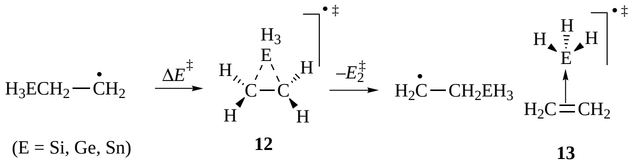
The (valence) double-ζ pseudopotential basis sets of Hay and Wadt[17] supplemented with a single set of d-type polarisation functions were used for the heteroatoms in this study [exponents $d(\zeta)_{Si} = 0.284$,[18] $d(\zeta)_{Ge} = 0.230$[18] and $d(\zeta)_{Sn} = 0.200$] while the double-ζ all-electron basis sets of Dunning and Hay[19] with an additional set of polarisation functions [exponents $d(\zeta)_C = 0.75$ and $p(\zeta)_H = 1.00$] were used for C, H, N and O. We refer to this basis set as DZP throughout this work.[13,20]

Calculations were performed on a Sun Sparcserver 10/512, DEC AlphaStation 400 4/233, DEC AlphaServer 8400, Cray Y-MP4E/364 or Cray J916 computer.

Results and discussion

(1,2)-Translocations between carbon centres. Degenerate rearrangement of the 2-silylethyl, 2-germylethyl and 2-stannylethyl radicals

Hypervalent species (**12**) of C_s symmetry were located on the C_2H_7E (E = Si, Ge, Sn) potential energy surfaces at the SCF/DZP and MP2/DZP levels of theory. These structures were found to correspond to the transition states for the degenerate rearrangement of the 2-silylethyl, 2-germylethyl and 2-stannylethyl radicals (Scheme 3). Calculated geometries of structures (**12**) are displayed in Fig. 1, while the calculated energy barriers ($\Delta E^‡$) are listed in Table 1, together with the calculated (single imaginary) vibrational frequency (ν) associated with the reaction coordinate in each case. Calculated energies of all structures in this study are found in Table 2.



Scheme 3

Fig. 1 reveals that the heteroatoms in transition states (**12**) appear to adopt tetrahedral arrangements of ligands. Indeed, structures **12** appear to resemble ‘coordinated alkenes’ (**13**), rather than the trigonal bipyramidal hypervalent structure † suggested by Walton and co-workers[9] for the transition state involved in the rearrangement of trialkylsilylaminyl radicals and are in agreement with the structure (**11**) proposed for homolytic rearrangements by the front-side mechanism. As expected, the carbon–heteroatom distances increase in moving down the group. MP2/DZP calculations predict separations of 2.051 (Si), 2.148 (Ge) and 2.317 Å (Sn), with corresponding SCF distances some 0.03–0.04 Å longer than the MP2 value in each case. Interestingly, the C–C distance is found to vary in the narrow range of 1.472–1.476 Å (MP2/DZP) and is relatively unaffected by the heteroatom. These geometric restrictions lead to severe C–E–C angles which range from 37.1 (Sn) to 42.1° (Si). It is interesting to compare the distances in **12** with those calculated at the same level of theory for the (pseudo) transition states ‡ involved in the degenerate attack of methyl radical at methylsilane, germane and stannane by the back-side mechanism.[13] Carbon–heteroatom distances of 2.058, 2.153 and 2.308 Å are calculated at the MP2/DZP level of theory for structures involving silicon, germanium and tin respectively.

As was observed in some calculations involving intermolecular homolytic substitution at group (IV) heteroatoms,[13] (1,2)-translocation of the germyl group is predicted to proceed with a higher energy barrier ($\Delta E^‡$) than the similar processes involving silicon and tin at all levels of theory. This trend is most pronounced at the SCF/DZP + ZPVE level, where values of $\Delta E^‡$ range from 103.9 (Si), to 136.3 (Ge) and 101.6 kJ mol^{-1} (Sn). Inclusion of electron correlation serves to reduce these barriers somewhat. At the MP2/DZP + ZPVE level, the calculated energy barriers are 96.4, 97.7 and 70.8 kJ mol^{-1} for reactions involving silicon, germanium and tin respectively. Inclusion of further (single-point) electron correlation (QCISD/DZP//MP2/DZP) has only slight effects on the calculated values of $\Delta E^‡$, with values of 103.0 (Si), 103.2 (Ge) and 74.6 kJ mol^{-1} (Sn). These data show a pleasing level of convergence

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† Eqn. (3) in ref. 9.

‡ Structures of C_{3v} symmetry were located on the Me_2EH_3 potential energy surfaces (E = Si, Ge, Sn) at the MP2/DZP level of theory. These structures proved to correspond to hypervalent intermediates on further analysis, however, when zero-point vibrational energy correction was included, barriers to dissociation effectively vanished.

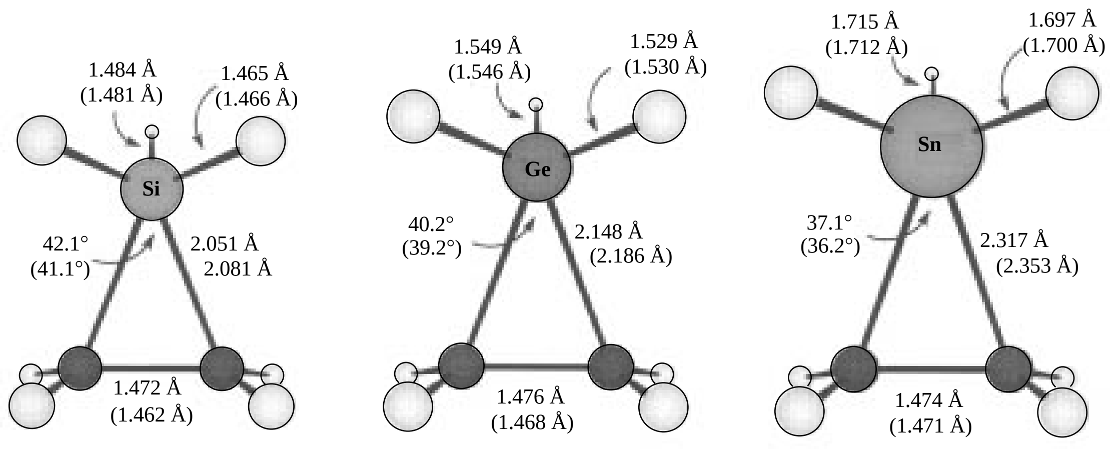


Fig. 1 MP2/DZP calculated structures and important geometric features of transition states (**12**) involved in homolytic (1,2)-translocation reactions of silyl (SiH_3), germyl (GeH_3) and stannyl (SnH_3) group in 2-silylethyl, 2-germylethyl and 2-stannylethyl radicals. (SCF/DZP data in parentheses.)

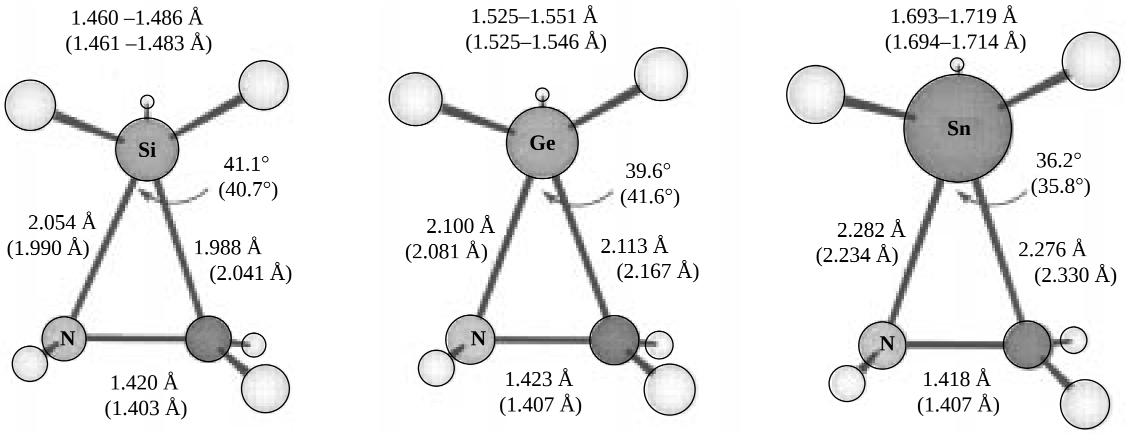


Fig. 2 MP2/DZP calculated structures and important geometric features of transition states (**14**) involved in homolytic (1,2)-translocation reactions of silyl (SiH_3), germyl (GeH_3) and stannyl (SnH_3) groups in (silylmethyl)aminyl, (germylmethyl)aminyl and (stannylmethyl)aminyl radicals. (SCF/DZP data in parentheses.)

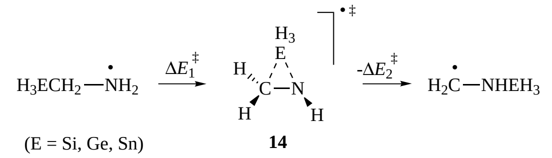
between the MP2 and QCISD (single-point) data, suggesting that MP2-levels of correlation are sufficient to provide reliable data.

It is instructive to compare these data with those obtained for the degenerate substitution by methyl radical at methylsilane, germane and stannane.[13] QCISD/DZP//MP2/DZP calculations predict energy barriers of 105.3, 103.5 and 86.9 kJ mol^{-1} for attack at silicon, germanium and tin respectively. The work summarized in this paper provides barriers for (1,2)-translocations between carbon centres which are similar in magnitude to the analogous intermolecular (back-side attack) reactions. We must therefore conclude these intramolecular reactions to be unlikely.

Rzepa and co-workers reported the results of a similar MNDO study which predicted an energy barrier of 200 kJ mol^{-1} for the (1,2)-translocation of SiH_3 between carbon centres.[21] It is likely that MNDO performs poorly for reactions of this type because of the lack of electron-correlation in the calculation, as well as the well known tendency of MNDO to overestimate strain energy,[22] which would be expected to be significant in transition states (**12**).

(1,2)-Translocations from carbon to nitrogen. Rearrangement of (silylmethyl)aminyl, (germylmethyl)aminyl and (stannylmethyl)aminyl radicals

Extensive searching of the CH_6NE (E = Si, Ge, Sn) potential energy surfaces at the SCF/DZP and MP2/DZP levels of theory located structures (**14**) as transition states for the (1,2)-translocation of SiH_3, GeH_3 and SnH_3 from carbon to nitrogen in the (silylmethyl)aminyl, (germylmethyl)aminyl and (stannylmethyl)aminyl radicals respectively (Scheme 4). Structures (**14**) proved to be of C_1 symmetry and are displayed in Fig. 2, while energy barriers for the forward ($\Delta E_1^{\ddagger}$) and reverse ($\Delta E_2^{\ddagger}$) reactions are listed in Table 3 together with the (single imaginary) frequency (ν) in **14**. Calculated energies of all structures in this study are found in Table 2.



Scheme 4

Inspection of Fig. 2 reveals, that like their carbon analogues (**12**), transition states (**14**) resemble 'coordinated imines'. The predicted degree of 'lateness' of the transition states (**14**) is dependent on the level of theory and the heteroatom involved. In all cases, inclusion of electron correlation (MP2) affords 'earlier' transition states, consistent with lower values of $\Delta E_1^{\ddagger}$ calculated using MP2/DZP (see later). For example, in the rearrangement of the (silylmethyl)aminyl radical, at the SCF/DZP level of theory, the N–Si separation in the transition state, at 1.990 Å is calculated to be slightly shorter than the C–Si distance (2.041 Å). This trend is reversed at the MP2/DZP level, with N–Si and C–Si separations calculated to be 2.054 and 1.988 Å respectively. This reversal of lengths is not observed in the case of germanium, both levels of theory predict the N–Ge distance in **14** [2.100 (MP2); 2.081 Å (SCF)] to be shorter than the C–Ge distance [2.113 (MP2); 2.167 Å (SCF)]. This reversal

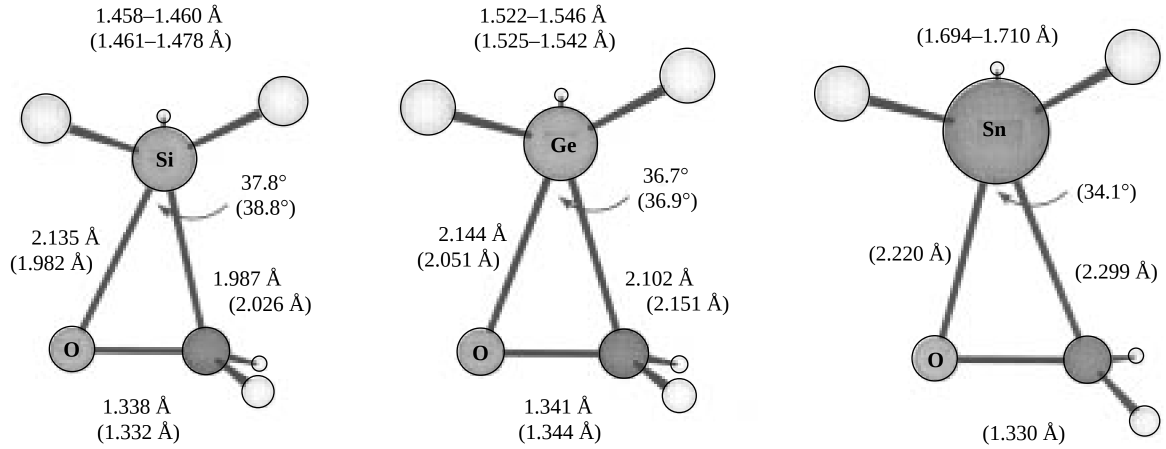


Fig. 3 MP2/DZP calculated structures and important geometric features of transition states (**15**) (SCF/DZP structure of **15**: E = Sn, see text) involved in homolytic (1,2)-translocation reactions of silyl (SiH_3), germyl (GeH_3) and stannyl (SnH_3) groups in silylmethoxyl, germylmethoxyl stannylmethoxyl radicals. (SCF/DZP data in parentheses.)

Table 1 Calculated energy barriers[a] ($\Delta E^‡$) for the degenerate (1,2)-translocation of SiH_3, GeH_3 and SnH_3 in 2-silylethyl, 2-germylethyl and 2-stannylethyl radicals ($H_3ECHCH_2^•$, Scheme 3) and the single imaginary frequency[b] (ν) associated with the transition states (**12**)

E	Method	$\Delta E^‡$	$\Delta E^‡$ + ZPVE	ν(TS)
Si	SCF/DZP	105.5	103.9	658i
	MP2/DZP	96.0	96.4	540i
	QCISD/DZP[c]	103.0	—	—
Ge	SCF/DZP	136.7	136.3	738i
	MP2/DZP	98.4	97.7	590i
	QCISD/DZP[c]	103.2	—	—
Sn	SCF/DZP	101.6	101.6	615i
	MP2/DZP	71.1	70.8	500i
	QCISD/DZP[c]	74.6	—	—

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

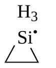
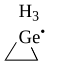
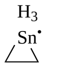
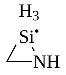
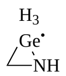
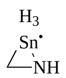
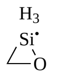
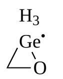
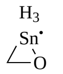
is also observed in the case of tin [N–Sn: 2.282 (MP2), 2.234 Å (SCF); C–Sn: 2.276 (MP2), 2.330 Å (SCF)]. The C–N separations in structures (**14**) are relatively unaffected by the nature of the heteroatom undergoing translocation. Not surprisingly, small N–E–C angles are predicted at both levels of theory; these range from 35.8 (Sn, SCF) to 41.6° (Ge, SCF).

Inspection of Table 3 reveals the calculated trends in the energy barriers ($\Delta E_1^‡$, $\Delta E_2^‡$). For example, at the SCF/DZP level the predicted energy barriers for the migration of SiH_3, GeH_3 and SnH_3 to nitrogen ($\Delta E_1^‡$) are 110.2, 111.1 and 74.0 kJ mol^{-1} respectively. Inclusion of electron correlation at the MP2 level (MP2/DZP) serves to reduce these barriers significantly to values of 50.8 (Si), 55.9 (Ge) and 28.2 (Sn) kJ mol^{-1}. Further (single-point) correlation correction (QCISD) results in increases in $\Delta E_1^‡$ by some 10–13 kJ mol^{-1} to 63.2 (Si), 68.8 (Ge) and 39.1 (Sn) kJ mol^{-1}. Inclusion of zero-point vibrational correction at the SCF and MP2 levels is shown to result in only marginal changes to $\Delta E_1^‡$. These translocation reactions are predicted to be exothermic at all levels of theory, with barriers for the reverse reaction ($\Delta E_2^‡$) ranging from 75.0 (Sn, QCISD) to 157.1 kJ mol^{-1} (Si, SCF/DZP + ZPVE).

Interestingly, reactions involving radical attack at germanium are, once again, predicted to have the highest (forward) energy barriers, as are the analogous translocations from carbon to oxygen at the QCISD level of theory (see later). The implications of these predictions are discussed below.

There is a pleasing level of agreement between these calculated data and those available experimentally. Walton and coworkers have determined by EPR techniques energy barriers of between 44 and 58 kJ mol^{-1} for the (1,2)-migration of the trimethylsilyl group from carbon to nitrogen in several substituted

Table 2 SCF, MP2 and QCISD calculated energies[a] of the reactants, products and transition states (**12**–**15**) in this study

Structure	SCF/DZP	MP2/DZP	QCISD/DZP[b]
$H_3SiCH_2CH_2^•$	−83.555 29	−83.914 66	−83.967 37
$H_3GeCH_2CH_2^•$	−83.417 58	−83.775 34	−83.827 42
$H_3SnCH_2CH_2^•$	−83.001 36	−83.352 62	−83.404 17
$H_3SiCH_2NH^•$	−99.555 33	−99.930 84	−99.982 33
$H_3GeCH_2NH^•$	−99.417 72	−99.791 89	−99.842 73
$H_3SnCH_2NH^•$	−99.001 95	−99.370 20	−99.420 43
$H_3SiCH_2O^•$	−119.390 65	−119.765 16	−119.815 54
$H_3GeCH_2O^•$	−119.253 40	−119.627 57	−119.677 20
$H_3SnCH_2O^•$	−118.838 63	n.d[c]	n.d[c]
$H_3SiNHCH_2^•$	−99.572 85	−99.958 31	−100.003 87
$H_3GeNHCH_2^•$	−99.426 70	−99.812 28	−99.856 97
$H_3SnNHCH_2^•$	−99.010 52	−99.390 09	−99.434 09
$H_3SiOCH_2^•$	−119.416 70	−119.807 26	−119.847 61
$H_3GeOCH_2^•$	−119.267 60	−119.659 06	−119.698 40
$H_3SnOCH_2^•$	−118.855 05	−119.240 43	−119.279 07
 (TS)	−83.515 10	−83.878 11	−83.928 16
 (TS)	−83.365 51	−83.737 87	−83.788 13
 (TS)	−82.962 66	−83.325 56	−83.375 78
 (TS)	−99.513 35	−99.911 50	−99.958 26
 (TS)	−99.375 42	−99.770 62	−99.816 52
 (TS)	−98.973 78	−99.359 46	−99.405 54
 (TS)	−119.356 75	−119.757 09	−119.802 50
 (TS)	−119.220 34	−119.619 69	−119.662 61
 (TS)	−118.819 95	n.d[c]	n.d[c]

[a] Energies in hartrees (1 E_h = 2626 kJ mol^{-1}). [b] QCISD/DZP//MP2/DZP. [c] Not determined, see text.

Table 3 Calculated energy barriers[a] for the forward ($\Delta E_1^{\ddagger}$) and reverse ($\Delta E_2^{\ddagger}$) (1,2)-translocation reactions of SiH_3, GeH_3 and SnH_3 in (silylmethyl)aminyl, (germylmethyl)aminyl and (stannylmethyl)aminyl radicals ($H_3ECHNH^{\bullet}$, Scheme 4) and the single imaginary frequency[b] (ν) associated with the transition states (**14**)

E	Method	$\Delta E_1^{\ddagger}$	$\Delta E_1^{\ddagger}$ + ZPVE	$\Delta E_2^{\ddagger}$	$\Delta E_2^{\ddagger}$ + ZPVE	ν(TS)
Si	SCF/DZP	110.2	110.5	156.2	157.1	667i
	MP2/DZP	50.8	51.1	122.9	122.5	455i
	QCISD/DZP[c]	63.2	—	119.8	—	—
Ge	SCF/DZP	111.1	110.7	134.7	135.0	644i
	MP2/DZP	55.9	55.7	109.4	108.7	464i
	QCISD/DZP[c]	68.8	—	106.2	—	—
Sn	SCF/DZP	74.0	73.9	96.5	97.6	508i
	MP2/DZP	28.2	28.4	80.4	80.4	344i
	QCISD/DZP[c]	39.1	—	75.0	—	—

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

Table 4 Calculated energy barriers[a] for the forward ($\Delta E_1^{\ddagger}$) and reverse ($\Delta E_2^{\ddagger}$) (1,2)-translocation reactions of SiH_3, GeH_3 and SnH_3 in silylmethoxyl, germylmethoxyl and stannylmethoxyl radicals ($H_3ECHO^{\bullet}$, Scheme 5) and the single imaginary frequency[b] (ν) associated with the transition states (**15**)

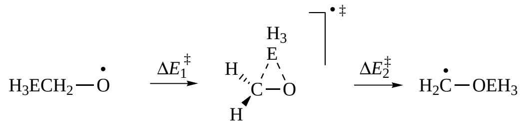
E	Method	$\Delta E_1^{\ddagger}$	$\Delta E_1^{\ddagger}$ + ZPVE	$\Delta E_2^{\ddagger}$	$\Delta E_2^{\ddagger}$ + ZPVE	ν(TS)
Si	SCF/DZP	89.0	86.6	157.4	157.8	624i
	MP2/DZP	21.2	19.9	131.7	130.7	369i
	QCISD/DZP[c]	34.2	—	118.5	—	—
Ge	SCF/DZP	86.8	83.9	124.1	124.0	579i
	MP2/DZP	20.7	19.7	103.4	102.9	325i
	QCISD/DZP[c]	38.3	—	94.0	—	—
Sn[d]	SCF/DZP	49.1	47.0	92.2	92.8	495i

[a] Energies in kJ mol^{-1}. [b] Frequencies in cm^{-1}. [c] QCISD/DZP//MP2/DZP. [d] MP2/DZP data not available, see text.

aminyl radicals.[9] Our (correlated) data for the analogous migration of SiH_3 in the (silylmethyl)aminyl radical include energy barriers of 50.8 (MP2/DZP) and 63.2 kJ mol^{-1} (QCISD/DZP//MP2/DZP). The close agreement between these calculated data and those obtained by EPR spectroscopy provides confidence in our ability to model (1,2)-translocation reactions by *ab initio* molecular orbital theory.

(1,2)-Translocations from carbon to oxygen. Rearrangement of silylmethoxyl, germylmethoxyl and stannylmethoxyl radicals (the radical Brook rearrangement)

Structures (**15**) of C_s symmetry were located on the CH_5EO (E = Si, Ge) potential energy surfaces at the SCF/DZP and MP2/DZP levels of theory. These structures proved to correspond to the transition states for the (1,2)-translocation of SiH_3 and GeH_3 from carbon to oxygen (Scheme 5), the reaction involving silicon being the prototypical radical Brook rearrangement.[2] In the rearrangement involving tin, the transition state (**15**: E = Sn) was located at the SCF/DZP level of theory. At the higher (MP2) level, neither transition state (**15**) nor the (starting) stannylmethoxyl radical ($H_3SnCH_2O^{\bullet}$) could be located as stationary points on the CH_5SnO energy surface. Calculated structures (**15**) are displayed in Fig. 3, while energy barriers for the forward and reverse reactions ($\Delta E_1^{\ddagger}$, $\Delta E_2^{\ddagger}$) are listed in Table 4 together with the (single imaginary) frequency (ν) in transition states (**15**). Calculated energies of all structures can be found in Table 2.



(E = Si, Ge, Sn) **15**

Scheme 5

As previously observed, the degree of 'lateness' of transition states (**15**) is dependent on the level of theory employed. For example, SCF/DZP calculations predict the O–Si separation in **15** to be 1.982 Å, somewhat shorter than the C–Si distance, which is calculated to be 2.026 Å. As was observed in the nitrogen-containing transition states (**14**), this trend is reversed at the MP2/DZP level, with O–Si and C–Si distances of 2.135 and 1.987 Å respectively. In other words, the (1,2)-translocation of SiH_3 from carbon to oxygen is predicted to be slightly later when electron correlation is included in the calculation. As observed for reactions involving **14**, these data are consistent with the lower values of $\Delta E_1^{\ddagger}$ obtained using MP2/DZP (see later) and is also observed in the transition state (**15**) involved in the transfer of GeH_3 where SCF/DZP predicts O–Ge and C–Ge separations of 2.051 and 2.151 Å respectively, while MP2/DZP calculations provide values of 2.144 and 2.102 Å for the same two parameters. The transition state (**15**) involved in the transfer of SnH_3 is predicted to have O–Sn and C–Sn distances of 2.220 and 2.299 Å respectively at the lower level. With C–O distances in structures (**15**) calculated to be between 1.330 and 1.34 Å, small C–E–O angles would be expected; these lie in the range 34.1–38.8°.

Table 4 clearly reveals that the (1,2)-translocations of silyl, germyl and stannyl groups from carbon to oxygen (Scheme 5) are more facile than the analogous translocations to nitrogen (Scheme 4) or between carbons (Scheme 3). Energy barriers ($\Delta E_1^{\ddagger}$) of between 19.7 kJ mol^{-1} (Ge, MP2/DZP + ZPVE) and 89.0 kJ mol^{-1} (Si, SCF/DZP) are calculated for the forward reactions, while the reverse reactions are predicted to proceed with barriers ($\Delta E_2^{\ddagger}$) which range from 92.2 (Sn, SCF/DZP) and 157.8 kJ mol^{-1} (Si, SCF/DZP + ZPVE). These (1,2)-translocations are, once again, found to be highly exothermic, as expected.

It is instructive to focus our attention on the prototypical radical Brook rearrangement as several reactions of this type have been reported. It is clear that SCF/DZP calculations overestimate the barrier to rearrangement (89.0 kJ mol^{-1}) for this reaction, as they do for rearrangements to nitrogen and may well do for the other rearrangements in this study. As found in the aminyl series, inclusion of electron correlation appears to be crucial in providing reliable data for (1,2)-translocations. Barriers of 19.9 and 34.2 kJ mol^{-1} are predicted using MP2/DZP + ZPVE and QCISD/DZP respectively. These values of $\Delta E_1^{\ddagger}$ are consistent with the rapidity of the radical Brook rearrangement reported in the literature.[2]

Finally, the prediction that the rearrangement of the stannylmethoxy radical proceeds without barrier at the MP2/DZP level of theory deserves some attention. These calculations suggest that $H_3SnCH_2O^{\bullet}$ does not correspond to an energy minimum and is therefore a non-isolable, non-observable species. In the other rearrangements involving tin (above), the (forward) barriers are predicted to decrease by 30–60 kJ mol^{-1} upon inclusion of electron correlation. This trend is also apparent in translocations to oxygen, where MP2 values of $\Delta E_1^{\ddagger}$ are lower than the corresponding SCF data by 65.8 (Si) and 66.1 (Ge) kJ mol^{-1}. As the SCF/DZP value of $\Delta E_1^{\ddagger}$ associated with the translocation to oxygen of SnH_3 is calculated to be 49.1 kJ mol^{-1}, inclusion of correlation would be expected to lead to barriers close to zero. What appears to be a somewhat surprising result on first inspection, is consistent with the trends observed in the series.

Conclusions

There are several significant predictions arising from this work. These include the unlikelihood of homolytic (1,2)-translocations of silyl, germyl and stannyl groups between carbons, the predicted facile nature of analogous translocations from carbon to nitrogen and carbon to oxygen, and the prediction that the stannylmethoxyl radical rearranges to the stannyloxylmethyl species without barrier. At all levels of theory, the transition states (**12**–**15**) are predicted to adopt tetrahedral geometry at the group (IV) element, consistent with a front-side mechanism for migration in which chiral group (IV) groups would be expected to migrate with retention of configuration.

Finally, it is worth noting that Kim recently reported that (1,6)-translocations involving trialkylgermanium substituents appear to proceed less readily than their silicon or tin counterparts.[4] Not unrelated to these observations are calculated data which predict that all (1,2)-translocations involving GeH_3 studied in this work have larger (forward) barriers than the analogous silicon or tin rearrangements at the highest level of theory.

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