

Reversibility in free-radical reactions of aryltellurides with tributylstannyl, tributylgermyl and tris(trimethylsilyl)silyl radicals

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Abstract

¹H, ¹³C, ²⁹Si, ⁷⁷Se, ¹¹⁹Sn and ¹²⁵Te NMR spectroscopies reveal that methyl, primary and secondary alkyl radicals, generated through the reaction of aryltelluroalkanes (**4–9**) with tributyltin hydride, tributylgermanium hydride or tris(trimethylsilyl)silane) under standard radical conditions (benzene, AIBN) are capable of displacing tributylstannyl, tributylgermyl and tris(trimethylsilyl)silyl radicals from aryltellurotributylstannanes (**1, 2**), aryltellurotributylgermanes (**10, 11**) and aryltellurotris(trimethylsilyl)silanes (**13, 14**) respectively. These observations are in agreement with high-level ab initio molecular orbital studies. Calculations using a (valence) double- ζ pseudopotential basis set supplemented with polarization functions and with the inclusion of electron correlation (MP2/DZP) predict energy barriers for the displacement of stannyl (SnH₃), germyl (GeH₃) and trisilylsilyl ((H₃Si)₃Si) radicals by methyl, ethyl and *iso*-propyl radicals to lie between 22 and 39 kJ mol⁻¹, with reverse barriers of between 12 and 40 kJ mol⁻¹. Consequently, the use of aryltellurides as alkyl radical precursors together with (standard) chain-carrying reagents such as tributyltin hydride, tributylgermanium hydride and tris(trimethylsilyl)silane may be complicated with equilibria which may result in diminished reaction yields. © 1998 Elsevier Science S.A.

Keywords: Alkyl radicals; Molecular orbital studies; Energy barriers; Aryltellurides

1. Introduction

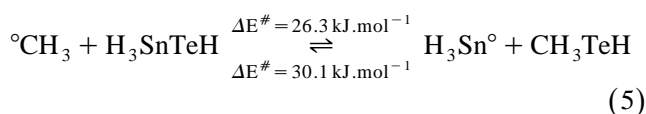
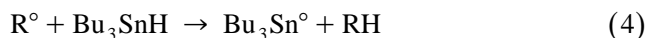
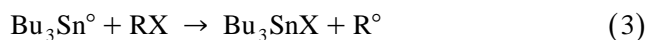
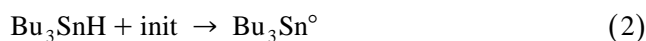
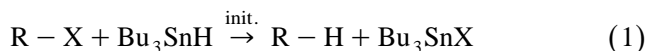
Free-radical chemistry currently enjoys unprecedented levels of popularity among synthetic chemists. This is undoubtedly due to current levels of understanding of the factors which govern the regio- and stereochemistry of free-radical processes which did not exist some 15–20 yrs ago and the ready availability of reagents and precursors tailor-made for free-radical reactions [1–11]. Indeed, the discovery that trialkyltin hydrides and alkyl halides react in a radical chain manner to afford the corresponding trialkyltin halide and alkane (Eq. 1) marks a major turning point in the development of radical techniques with synthetic applicability. Tributyltin hydride and to a lesser extent, triphenyltin hydride have been the reagents of choice [1]. Their ready availability and favourable rate constants for attack of the corresponding tin-centred radicals at the halogen atom in alkyl halides (ca. 10³–10⁹ M⁻¹ s⁻¹ (25°); Eq. 3), [12] coupled with useful rate

constants for hydrogen transfer [13–20] to alkyl radicals (ca. 10⁶ M⁻¹ s⁻¹ (25°); Eq. 4) provide for reagents superior to their silicon [21–27] and germanium [18,28,29] counterparts; only tris(trimethylsilyl)silane rivals trialkyltin hydrides in its synthetic utility [26,27]. A knowledge of rate constants is crucial to the successful design of synthetic procedures involving these reagents. Stannane chain-carrying reagents are useful because a knowledge of the rate constants associated with hydrogen transfer and halogen abstraction allow, through control of substrate concentration, necessary selectivity criteria to be met [1]. Today, many classes of free-radical precursor have been developed for use with chain-carrying reagents such as tributyltin hydride. More commonly used examples include dithio- and thionocarbonates, [30–32] pyridine-2-thioneoxycarbonyl (PTOC) esters, [30,33] imidate esters [34] and carbamates [35] as well as aryl sulfides, selenides and tellurides [12].

The ability to provide quality data relating to the intimate details of reaction mechanisms is of critical importance to their understanding. It is no accident that the increase in the level of understanding of intramolec-

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ular homolytic addition (ring-closure) chemistry provided by many workers over the last two decades has lead to the recent rapid increase in the use of that methodology in synthesis. The fine detail able to be provided by quality quantum computational data are unrivalled; in no other way can the geometry and electronic structure of transition states and unstable intermediates along reaction pathways be understood.



Our recent interest in the development of new homolytic substitution methods and modified stannanes for use in free-radical synthesis has been aided by the computer modelling of various homolytic substitution reactions through the use of ab initio molecular orbital theory. Of importance to the work described in this paper are the results of high-level ab initio investigations into the attack of silyl, germyl and stannyl radicals at the halogen atom in halomethanes [36] and the chalcogen atom in the analogous sulfides, selenides and tellurides [37,38]. These studies predict that, in accordance with expectation, [12] stannyl radicals react at the halogen or chalcogen atom in halo- and chalcogenomethanes in the following reactivity order: $\text{I} \geq \text{Te} > \text{Br} \geq \text{Se} > \text{Cl} \geq \text{S}$. Somewhat surprisingly, reactions at tellurium were calculated to be reversible. Calculations involving a (valence) double- ζ pseudopotential (DZP) basis set and electron correlation (MP2, QCISD) predict that stannyl radical ($\text{H}_3\text{Sn}^\circ$) undergoes reversible free-radical attack at the tellurium atom in methanetellurol (MeTeH) with expulsion of methyl radical (Eq. 5). Our MP2/DZP calculations provide energy barriers of 28.8 and 40.3 kJ mol^{-1} for the displacement of $\text{H}_3\text{Sn}^\circ$ by methyl radical and the reverse reaction respectively, while QCISD/DZP//MP2/DZP calculations give values of 26.3 and 30.1 kJ mol^{-1} for the same two reactions [37,38]. Intrigued by this apparently contra-intuitive result and given the increased use of aryltellurides as free-radical precursors, we began to explore the reaction of methyl and other radicals with phenyltellurotributylstannane and other group(IV)-containing tellurides. We now report that methyl, primary- and secondary- alkyl radicals are capable of displacing tributylstannyl, tributylgermyl and tris(trimethylsilyl)silyl radicals from

phenyltellurotributylstannane, phenyltellurotributylgermane and phenyltellurotris(trimethylsilyl)silane respectively, results which are consistent with ab initio molecular orbital calculations.

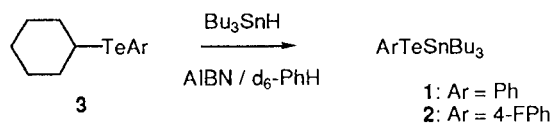
2. Results and discussion

2.1. Reactions involving phenyltellurotributylstannane and (4-fluorophenyl)tellurotributylstannane

Phenyltellurotributylstannane (**1**) and (4-fluorophenyl)tellurotributylstannane (**2**) were prepared by reaction of phenyltellurocyclohexane (**3**: Ar = Ph) [39] or (4-fluorophenyl)tellurocyclohexane (**3**: Ar = 4-FPh) [40] with tributyltin hydride in d_6 -benzene (AIBN initiator) (Scheme 1). The tellurides (**1**, **2**) proved to be light sensitive and generally unstable, attempted removal of the solvent resulted in rapid decomposition. In benzene, under nitrogen and in the dark, they appear to have an indefinite lifetime. Consequently, **1** and **2** were characterized by ^1H , ^{13}C , ^{119}Sn and ^{125}Te NMR spectroscopies. Specifically, **1** exhibits a singlet at $\delta - 1.3$ ppm in the ^{119}Sn NMR spectrum with satellite coupling to ^{125}Te [$J(^{119}\text{Sn}-^{125}\text{Te}) = 2693$ Hz], while the ^{125}Te NMR spectrum of **1** revealed a singlet at $\delta - 209.4$ ppm with the expected satellite coupling to ^{117}Sn and ^{119}Sn [$J(^{117}\text{Sn}-^{125}\text{Te}) = 2578$ Hz; $J(^{119}\text{Sn}-^{125}\text{Te}) = 2692$ Hz]. Similarly, **2** exhibits analogous signals: ^{119}Sn NMR $\delta 0.4$ [$J(^{119}\text{Sn}-^{125}\text{Te}) = 2656$ Hz]; ^{125}Te NMR $\delta - 213.9$ [$J(^{125}\text{Te}-^{117}\text{Sn}) = 2526$ Hz, $J(^{125}\text{Te}-^{119}\text{Sn}) = 2656$ Hz]. These spectroscopic data leave no doubt that the tellurostannanes (**1**, **2**) had indeed been prepared in situ.

When one equivalent of 4-fluorotelluroanisole (**4**) [41] (^{125}Te NMR, $\delta 342.8$), tributyltin hydride (5 mol%) and AIBN (5 mol%) were introduced into the NMR solution of **1** and the colourless solution heated at 80°C for 2 h, ^{119}Sn and ^{125}Te NMR spectroscopies revealed the presence of telluroanisole (**5**) [41] and **2**, in addition to starting material (Fig. 1) by comparison with authentic samples. Importantly, when **1** was heated at 80°C in benzene either in the absence of any reagents or in the presence of 4-fluorotelluroanisole (**4**) [41] and tributyltin hydride (5 mol%) with no initiator (AIBN), no reaction was observed by ^{119}Sn and ^{125}Te NMR spectroscopies after 2 h at 80°C .

We postulate that the formation of **2** and **5** involves homolytic substitution by methyl radical, generated by



Scheme 1.

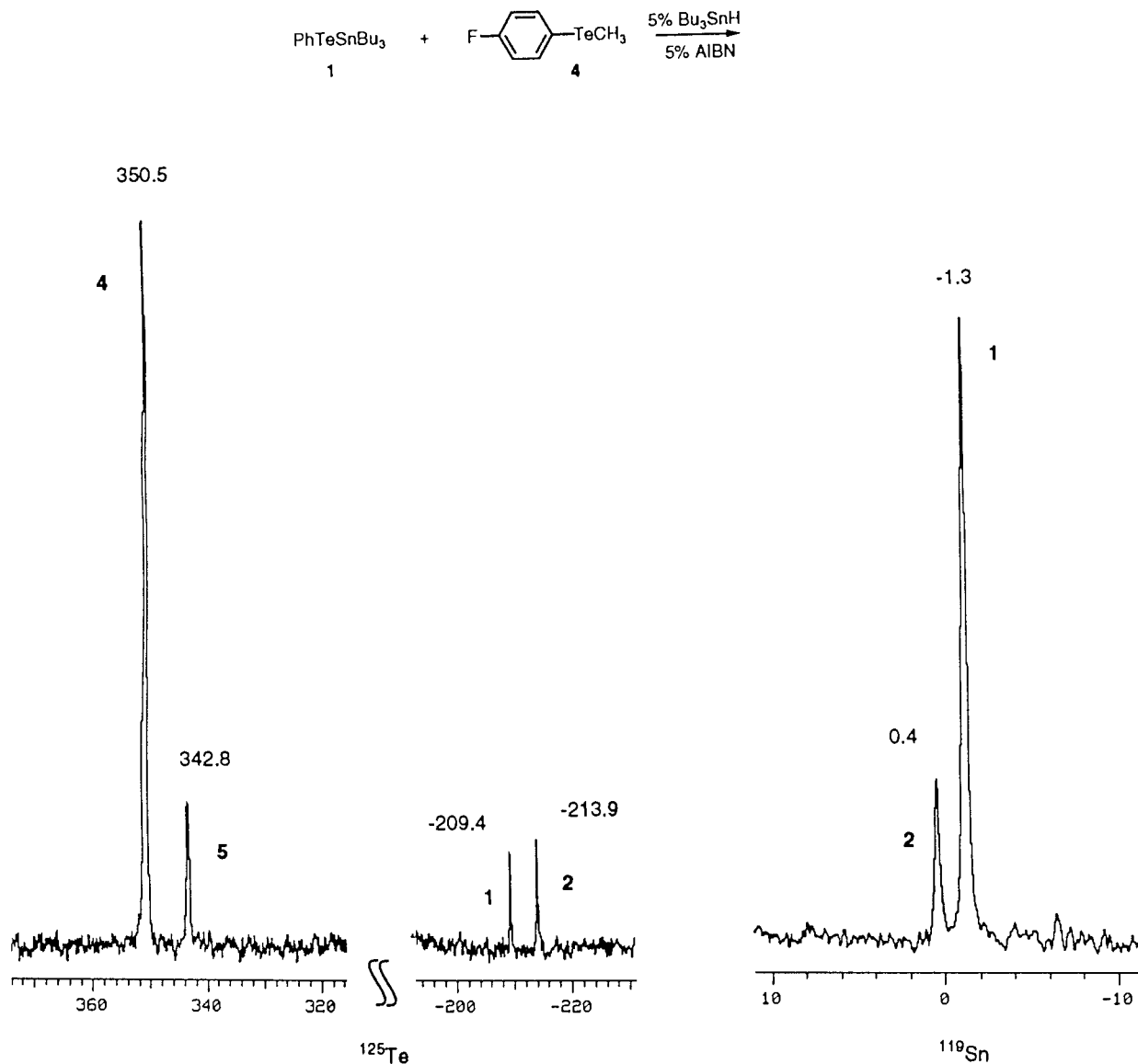


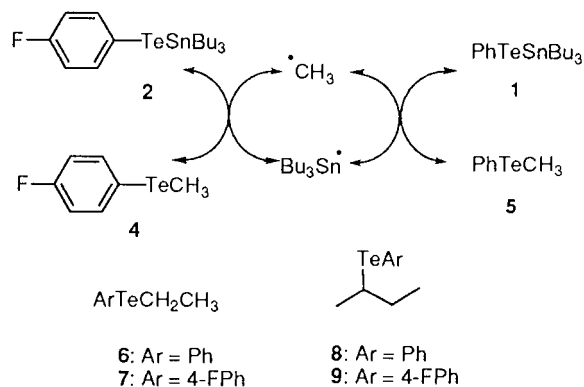
Fig. 1. ^{125}Te and ^{119}Sn NMR spectra (d_6 -benzene) of the reaction of **1** with **4** at 80° in the presence of 5% Bu_3SnH and 5% AIBN.

reaction of 4-fluorotelluroanisole (**4**) with tributylstannyl radical, at the tellurium atom in **1** with expulsion of further chain-carrying tributylstannyl radical (Scheme 2).

When the reaction was repeated using **2** and telluroanisole (**5**) as starting materials, ^{119}Sn and ^{125}Te NMR techniques revealed the presence of **1** and **4**, as expected on the basis of the mechanism depicted in Scheme 2.

The data presented so far are in agreement with our previous *ab initio* calculations (Eq. 5) and verify that methyl radical is capable of displacing stannyl radical from tellurium in organo-tellurides. Both experimentally-derived and computational data raise the question of the generality of these radical processes. Whether or not alkyl radicals in general are also capable of displacing chain-carrying species such as tributylstannyl radi-

cal from organo-tellurides assumes some importance given the increased usage of tellurides as radical precursors in synthesis. In order to shed further light on this



Scheme 2.

question, we set about examining reactions analogous to those described above using phenyltelluroethane (**6**) [42] and 4-fluorophenyltelluroethane (**7**), or 2-(phenylteluro)butane (**8**) [43] and 2-(4-fluorophenylteluro)butane (**9**) instead of **4** and **5**.

Tellurides (**4–9**) were prepared from the corresponding alkyl bromide or iodide and either diphenyl ditelluride [44] or di(4-fluorophenyl) ditelluride [44] according to standard procedures. [40] When tellurides **6** or **8** were reacted with (4-fluorophenyl)tellurotributylstannane (**2**) in the manner described previously, once again, ^{125}Te and ^{119}Sn NMR spectroscopies revealed the formation of phenyltellurotributylstannane (**1**) and tellurides **7** or **9** respectively. Typical ^{125}Te NMR spectra are displayed in Fig. 2. Similar reactions using **7** or **9** with **1** resulted in the formation of **2** as well as **6** or **8** respectively (Scheme 3). These results clearly indicate that primary and secondary alkyl radicals are also capable of displacing tributylstannyl radicals from tellurium.

2.2. Reactions involving phenyltellurotributylgermane and (4-fluorophenyl)tellurotributylgermane

Despite their widespread use in free-radical syntheses, trialkylstannanes often deliver hydrogen atom to alkyl radicals with rate constants too high for acceptable synthetic outcomes [1]. On occasion, despite the inherent expense, trialkylgermanes have replaced their tin counterparts; their lower rate constants for the delivery of hydrogen often lead to increased reaction yields, especially when the primary bond-forming reaction of interest (e.g., intramolecular homolytic addition) is slow [18,28,29].

We therefore turned our attention to the reactions of the germanium analogues of **1** and **2** with methyl, primary and secondary alkyl radicals with the intention of determining whether or not tributylgermyl radicals are also capable of reacting reversibly with alkyltellurides. Phenyltellurotributylgermane (**10**) and (4-fluo-

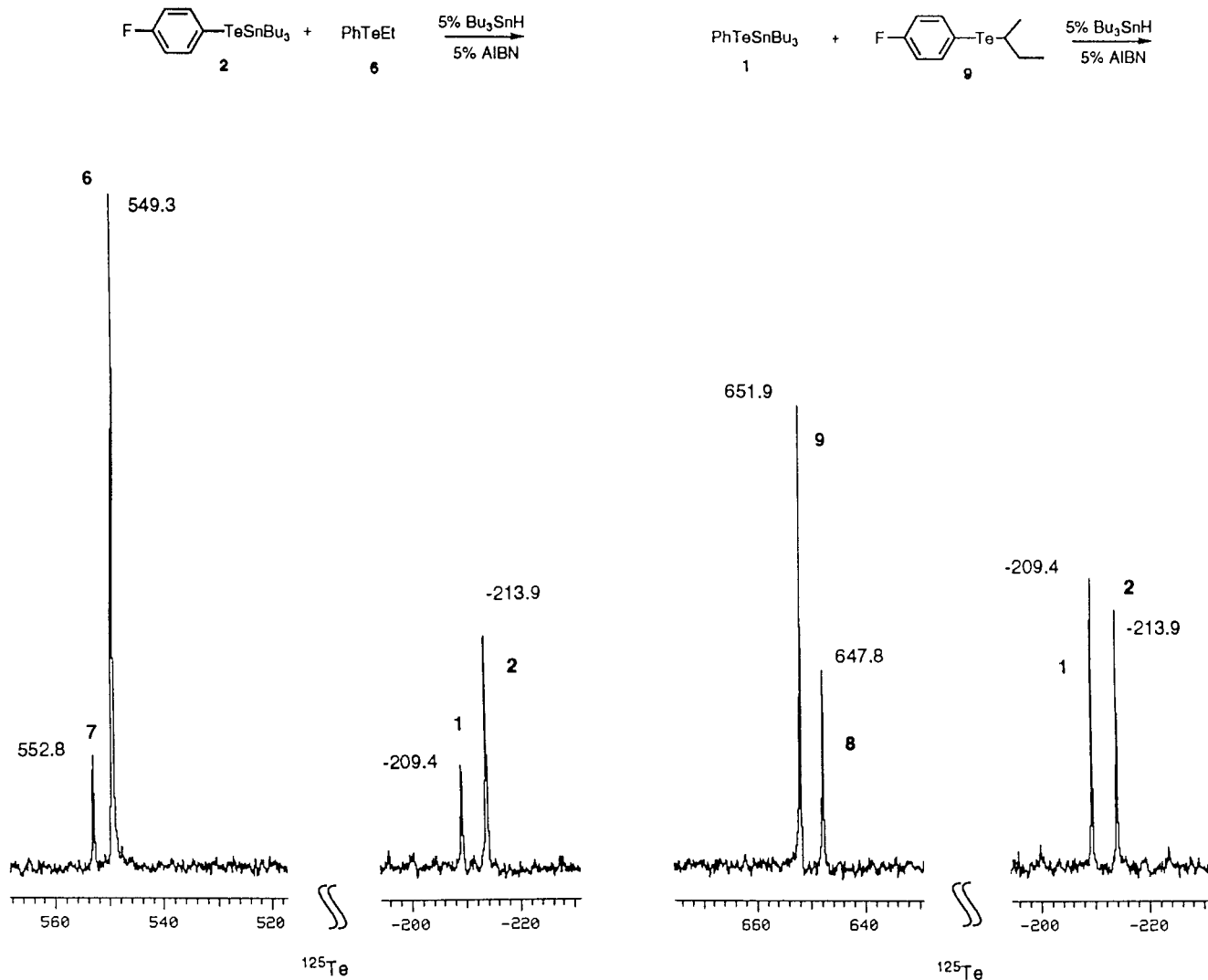
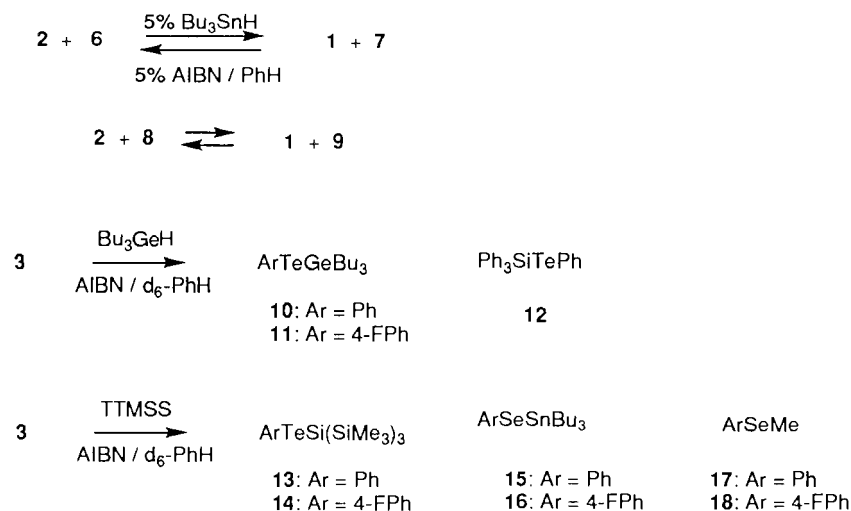


Fig. 2. ^{125}Te NMR spectra (d_6 -benzene) of the reaction of **2** with **6** (left); and **1** with **9** (right) at 80° in the presence of 5% Bu_3SnH and 5% AIBN.



Scheme 3.

rophenyl)tellurotributylgermane (**11**) were prepared in identical fashion to their tin counterparts, using tributylgermanium hydride and the appropriate aryltellurocyclohexane (**3**). As was observed for the tellurostannanes (**1**, **2**), the germanium analogues (**10**, **11**) proved to be light-sensitive and unstable; their preparation in situ was confirmed by careful ^1H , ^{13}C and ^{125}Te NMR monitoring of the reaction mixtures. Specifically, telluride (**10**) exhibits a singlet in the ^{125}Te NMR spectrum at $\delta -78.7$, while **11** displays the analogous singlet at $\delta -82.8$. When phenyltellurotributylgermane (**10**) was reacted with **5**, **7** or **9** and 5 mol% tributylgermanium hydride under identical conditions to those described for the reaction of the tin analogue (**1**), ^{125}Te NMR spectroscopy revealed the formation of (4-fluorophenyl)tellurotributylgermane (**11**) as well as **6**, **8** or **10** respectively. A typical ^{125}Te NMR spectrum is shown in Fig. 3. In addition, similar reactions using **11** as well as **6**, **8** or **10** as starting materials resulted in the formation of **10** together with **5**, **7** or **9** respectively.

Once again, these data confirm that methyl, primary, and secondary alkyl radicals are capable of displacing tributylgermyl radicals from tellurogermanes (**10**, **11**). These results strongly suggest that tributylgermyl radicals are able to react reversibly with alkyltellurides.

2.3. Reactions involving phenyltellurotris(trimethylsilyl)silane and (4-fluorophenyl)tellurotris(trimethylsilyl)silane

Trialkylsilanes are generally unsuitable reagents for use in free-radical syntheses due to their general inability to sustain chain reactions because of slow rates of transfer of hydrogen atom to alkyl radicals [26,27]. Our inability to prepare phenyltellurotriphenylsilane (**12**) through the reaction of triphenylsilane with phenyltellurocyclohexane demonstrates the inherent difficulties

associated with silanes in general. Tris(trimethylsilyl)silane (TTMSS) was developed specifically to overcome the poor chain propagation properties of silanes in general and as a reagent to replace trialkylstannanes which have undesirable toxicity and chromatographic properties [26,27,45]. Indeed, tris(trimethylsilyl)silane has been reported to behave much more like a stannane than a silane in free-radical chemistry [46].

It therefore came as no surprise that alkyl radicals proved to be capable of displacing tris(trimethylsilyl)silyl radicals from alkyltellurides (**13**, **14**). Once again, due to inherent stability problems, reagents were prepared in situ; phenyltellurotris(trimethylsilyl)silane (**13**) and (4-fluorophenyl)tellurotris(trimethylsilyl)silane (**14**) were prepared by the reaction TTMSS with the appropriate aryltellurocyclohexane (**3**). Tellurosilanes (**13**, **14**) were characterized by ^1H , ^{13}C , ^{29}Si and ^{125}Te NMR spectroscopy. Specifically, **13** exhibits a singlet at $\delta -192.9$ with satellite coupling to ^{29}Si [$J(^{125}\text{Te}-^{29}\text{Si}) = 135 \text{ Hz}$] in the ^{125}Te NMR spectrum and two singlets at $\delta -10.6$ and -94.4 , the latter displaying satellite coupling to ^{125}Te [$J(^{29}\text{Si}-^{125}\text{Te}) = 135 \text{ Hz}$], in the ^{29}Si NMR spectrum, while **14** exhibits a singlet at $\delta -195.9$ (^{125}Te), $\delta -10.6$ and -92.6 (^{29}Si).

When phenyltellurotris(trimethylsilyl)silane (**13**) was reacted with **5**, **7** or **9** and 5 mol% TTMSS under identical conditions to those described for the reaction of the tin analogue (**1**), ^{125}Te NMR spectroscopy revealed the formation of (4-fluorophenyl)tellurotris(trimethylsilyl)silane (**14**) as well as **6**, **8** or **10** respectively. A typical ^{125}Te NMR spectrum is shown in Fig. 3. Similarly, reactions using **14** together with **6**, **8** or **10** as starting materials resulted in the formation of **13** together with **5**, **7** or **9** respectively.

Once again, these data confirm that methyl, primary, and secondary alkyl radicals are capable of displacing

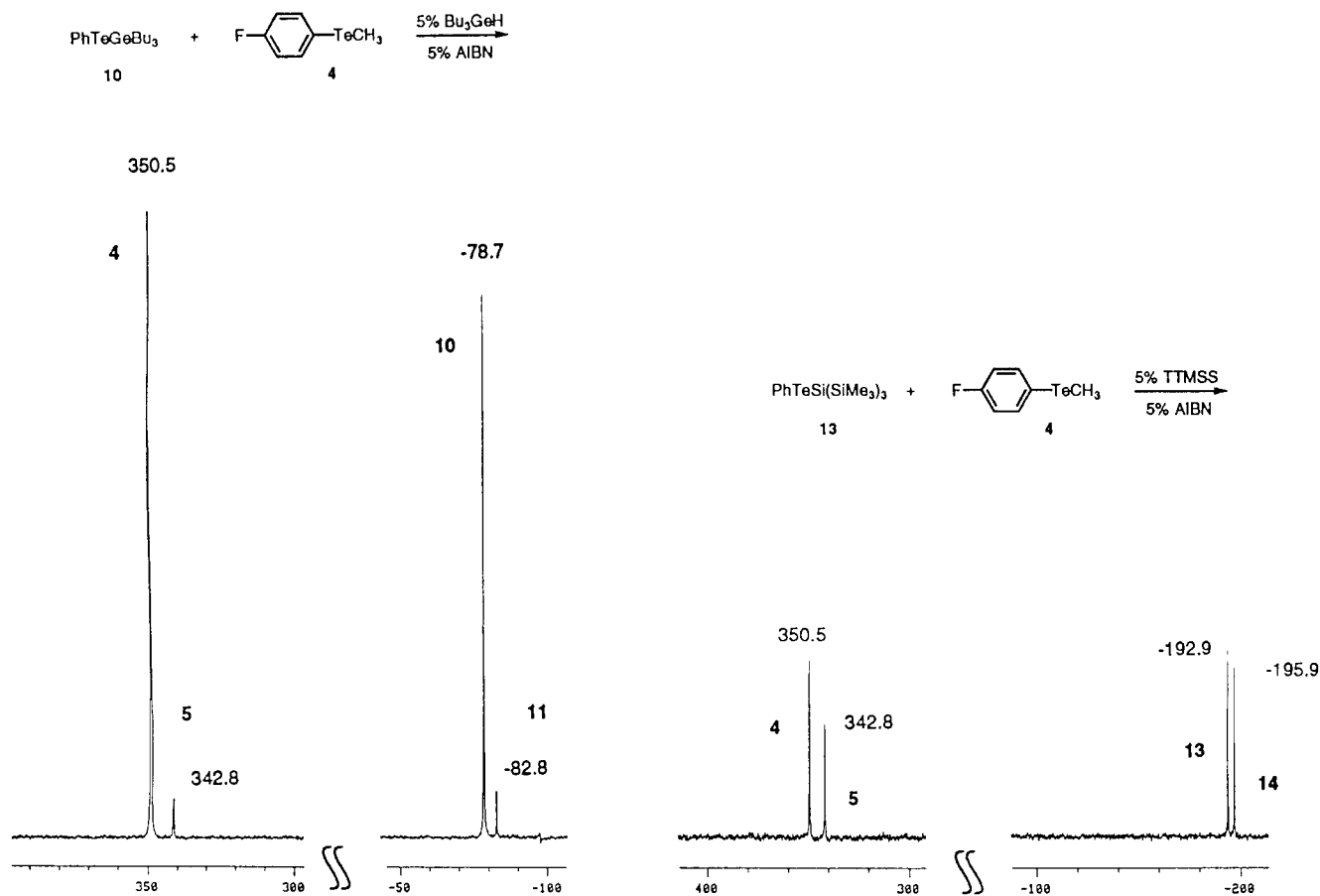


Fig. 3. ^{125}Te NMR spectra (d_6 -benzene) of the reaction of **10** with **4** at 80° in the presence of 5% Bu_3GeH and 5% AIBN (left); and **13** with **4** at 80° in the presence of 5% TTMS and 5% AIBN (right).

tris(trimethylsilyl)silyl radicals from tellurosilanes (**13**, **14**). These results strongly suggest that, as was demonstrated for tributylstannyl and germyl radicals tris(trimethylsilyl)silyl radicals are also able to react reversibly with alkyltellurides. These results are also of significance in inorganic chemistry, especially given the recent importance of tris(trimethylsilyl)selenides and tellurides in inorganic synthesis [47–50].

2.4. Reactions involving phenylselenotributylstannane and (4-fluorophenyl)selenotributylstannane

Given the widespread use of alkylselenides as free-radical precursors, we chose to examine whether or not tributylstannyl radicals react reversibly with alkyl selenides. To that end, phenylselenotributylstannane [**51**] (**15**) and (4-fluorophenyl)tellurotributylstannane [**51**] (**16**) were prepared by reaction of phenylselenocyclohexane [**51**] and (4-fluorophenyl)selenocyclohexane with tributyltin hydride under standard conditions. Despite being air-stable solids, [**51**] we chose to prepare solutions in identical fashion to those prepared for the tellurium analogues (**1**, **2**). These solutions were characterized by ^{77}Se and ^{119}Sn NMR spectroscopies. Specifi-

cally, **15** displays a singlet at $\delta -23.3$ in its ^{77}Se NMR spectrum, while **16** exhibits the analogous signal at $\delta -32.3$. In addition, ^{119}Sn NMR spectroscopy revealed singlets at $\delta 57.8$ and 59.6 for **15** and **16** respectively.

When selenoanisole (**17**), tributyltin hydride (5 mol%) and AIBN (5 mol%) were introduced into a benzene solution of **16** and the resultant solution heated at 80°C for 2 h, both ^{77}Se and ^{119}Sn NMR spectroscopy revealed the presence of the selenostannane (**15**) in addition to starting materials (**16**, **17**) by comparison with authentic samples. Importantly, no 4-fluorotelluroanisole (**18**) was observed. It seems likely that selenostannane (**15**) arises by homolytic substitution of tributylstannyl radicals generated from tributyltin hydride (AIBN) at the selenium atom in **17** with expulsion of methyl radical. These methyl radicals, in turn abstract hydrogen atom from the stannane in preference to attacking the selenium atom in **16**.

Similar results are obtained when **18** is reacted with **15**, namely **16** is observed in addition to starting material. From these data we conclude that under standard radical reaction conditions (i.e., tributyltin hydride, AIBN), methyl radicals are not capable of displacing tributylstannyl from tributylstannylselenides, strongly

suggesting that tributylstannyl radicals react irreversibly with alkyl selenides under these conditions.

2.5. *Ab initio* molecular orbital calculations

In order to shed further light on the ability of alkyl radicals to displace trialkylstannyl radicals from tellurostannanes (**1**, **2**), trialkylgermyl radicals from **10** and **11**, as well as the tris(trimethylsilyl)silyl moiety from tellurosilanes (**13** and **14**), we chose to examine the potential energy surfaces for the attack of ethyl and *iso*-propyl radicals at the tellurium atom in stannyltelluro (H_3SnTeH), germyltelluro (H_3GeTeH) and silyltelluro (H_3SiTeH), as well as attack of methyl radical at tris(trimethylsilyl)silyltelluro ($(\text{H}_3\text{Si})_3\text{SiTeH}$) with expulsion of the appropriate group(IV)-centred leaving radical (Scheme 4). Comparison of the data generated in this manner with those obtained in our previous study involving methyl radical, [37,38] as well as the experimental data should serve to provide significant insight into the nature of the reactions in question.

All *ab initio* molecular orbital calculations were carried out using the Gaussian 92 and 94 programs [52,53]. 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 [54]. 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.

The (valence) double- ζ pseudopotential basis sets of Wadt and Hay [55–57] supplemented with a single set of *d*-type polarisation functions were used for the het-

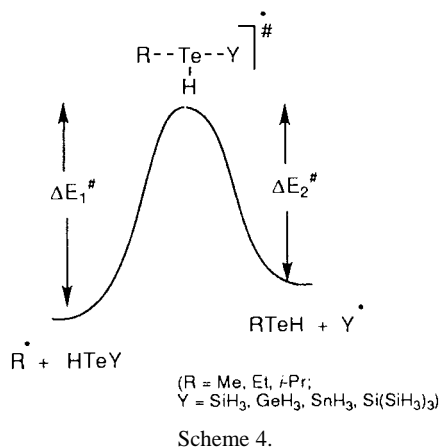
eroatoms in this study (exponents $d(\zeta)_{\text{Si}} = 0.284$, [58] $d(\zeta)_{\text{Ge}} = 0.230$, [58] $d(\zeta)_{\text{Sn}} = 0.200$, [59] $d(\zeta)_{\text{S}} = 0.60$, [55–57] $d(\zeta)_{\text{Se}} = 0.38$, [58] $d(\zeta)_{\text{Te}} = 0.30$ [58] while the double- ζ all-electron basis sets of Dunning [60] with an additional set of polarisation functions (exponents $d(\zeta)_{\text{C}} = 0.75$ and $p(\zeta)_{\text{H}} = 1.00$) were used for C, H, N and O. We refer to this basis set as DZP throughout this work [37,38,61].

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.

Extensive searching of the potential energy surfaces for the reactions depicted in Scheme 4 located hypervalent structures (**19–25**) at both SCF/DZP and MP2/DZP levels of theory. Vibrational frequency analysis revealed that these structures correspond to transition states for the displacement of the group(IV)-centred radical (Y) by alkyl radical (R) from tellurium. At the SCF/MP2 level, transition states (**19–25**) are predicted to be of C_s symmetry, while at the higher level (MP2/DZP), significant deviation from the collinear arrangement of attacking and leaving radicals found at the SCF level is predicted; all transition states adopt C_1 symmetry at MP2/DZP. Dihedral angles (R–Te–H–Y) of between 150° and 167° are predicted and are consistent with our previously published data for the similar reactions involving methyl radical [37,38]. These deviations from collinearity have been discussed in terms of a favourable interaction of the lone-pair electrons on chalcogen with the three-centre, three-electron ‘bond’ in transition states of this sort [62].

MP2/DZP—generated transition structures (**19–25**) are displayed in Fig. 4, while the calculated energy barriers for the forward and reverse reactions (ΔE_1^\ddagger , ΔE_2^\ddagger in Scheme 4) are listed in Table 1. Calculated energies of all structures in this study can be found in Table 2.

Inspection of Fig. 4 reveals a close similarity between the structures generated in this study to those in our previous study. For example, the C–Te separation in transition state **23**, at 2.437 Å (MP2) is slightly longer than the similar distance in **24**, at 2.411 Å at the same level of theory and somewhat shorter than the C–Te distance in the analogous transition state involving methyl radical (MeTe(H)SnH_3) at 2.457 Å (MP2/DZP) [37,38]. A corresponding lengthening of the Te–Sn distance is predicted, with MP2/DZP calculated distances of 2.859 Å when the attacking radical is methyl, [37,38] 2.886 Å (ethyl) and 2.906 Å (*iso*-propyl). Similar trends are predicted for the silyl and germyl containing transition states and are consistent with the increasing degree of ‘lateness’ expected in progressing from methyl to ethyl and *iso*-propyl radicals as attacking species. It is interesting to compare these data with those for transition state (**25**) in which



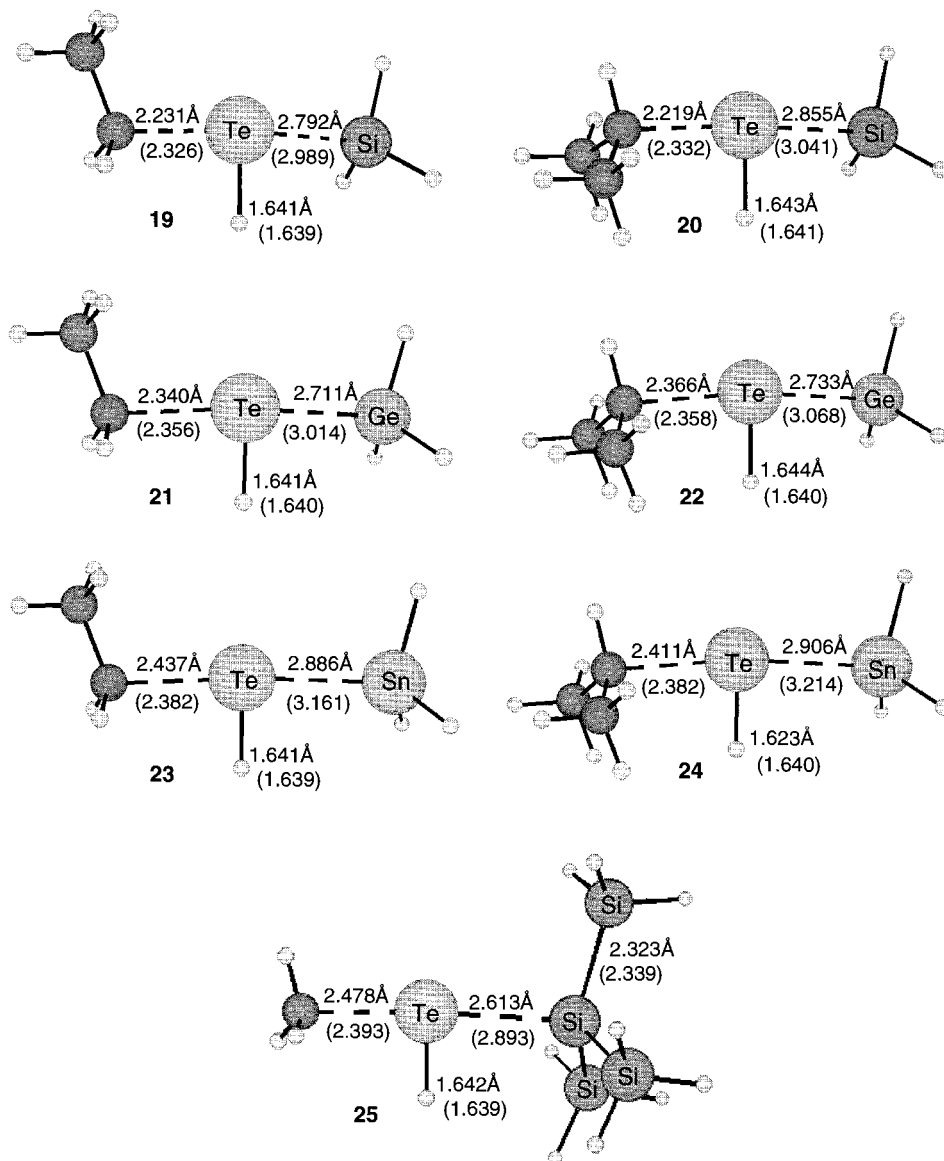


Fig. 4. MP2/DZP generated structures of transition states (19–25). (SCF/DZP data in parentheses).

the tris(trimethylsilyl)silyl radical is involved as the leaving species. The MP2/DZP calculated C–Te distance, at 2.478 Å, is significantly longer than the corresponding separation in the similar transition state involving SiH₃ (MeTe(H)SiH₃) which is calculated to be 2.393 Å [37,38]. Indeed, this distance resembles the C–Te distance in the reaction involving SnH₃ (MeTe(H)SnH₃) (2.489 Å) more closely. This result is interesting because, as previously mentioned, TTMSS often behaves more like a stannane than a silane, [46] an observation which has been extensively exploited in free-radical chemistry [1].

The calculated energy barriers presented in Table 1 also reveal some interesting trends. Firstly, the SCF/DZP generated data provide energy barriers which are significantly higher for the forward reactions in all cases than the corresponding MP2/DZP generated data.

In other related work, we have established that the inclusion of electron correlation is necessary in order to reliably model homolytic substitution reactions at a variety of main-group elements [12,37,38,59,61]. It is therefore not surprising that the SCF level of theory also models the reactions in this study poorly. Interestingly, the QCISD/DZP//MP2/DZP single-point data also diverge somewhat from the MP2-generated data. We believe that these differences are most likely to be due to the differences between the MP2/DZP and QCISD/DZP potential energy surfaces.¹ Unfortu-

¹ For example, Me₂Cl is predicted to be a transition state at both MP2/DZP and QCISD/DZP (fully optimized) levels of theory. The former calculations provides a C–Cl distance of 2.062 Å, while at the higher level this separation is predicted to be 2.117 Å. C.H. Schiesser and L.M. Wild, unpublished.

Table 1
SCF/DZP, MP2/DZP and QCISD/DZP//MP2/DZP calculated energy barriers^a for the forward (ΔE_1^\ddagger) and reverse (ΔE_2^\ddagger) reactions in this study (Scheme 4)

Radical (R)	TS	SCF		MP2		QCISD/MP2	
		ΔE_1^\ddagger	ΔE_2^\ddagger	ΔE_1^\ddagger	ΔE_2^\ddagger	ΔE_1^\ddagger	ΔE_2^\ddagger
Me·	MeTe(H)SiH ₃	92.9 ^b	36.5 ^b	37.6 ^b	19.1 ^b	37.2 ^b	9.6 ^b
Et·	[19]	100.5	31.8	38.9	13.5	46.0	9.4
<i>i</i> -Pr·	[20]	109.6	28.7	37.2	12.8	49.2	8.6
Me·	MeTe(H)GeH ₃	79.9 ^b	39.1 ^b	30.7 ^b	29.0 ^b	28.4 ^b	19.9 ^b
Et·	[21]	86.6	33.4	30.0	23.2	31.9	13.7
<i>i</i> -Pr·	[22]	95.0	29.8	26.0	20.2	32.7	10.7
Me·	MeTe(H)SnH ₃	74.4 ^b	41.1 ^b	28.8 ^b	40.3 ^b	26.3 ^b	30.1 ^b
Et·	[23]	80.6	36.1	26.8	33.2	27.8	22.6
<i>i</i> -Pr·	[24]	88.6	33.9	22.4	29.8	27.6	18.4
Me·	[25]	77.8	43.8	29.9	16.1	28.0	16.6

^aEnergies in kJ mol⁻¹.

^bTaken from [37,38].

nately, QCISD/DZP (full) optimizations on the structures in this study are tasks beyond our current resources.

As expected from previous calculations, reactions of alkyl radicals at silyltellurol (H₃SiTeH) with expulsion of SiH₃ are predicted to be endothermic. MP2/DZP calculations predict energy barriers (ΔE_1^\ddagger , Scheme 4) of 37–39 kJ mol⁻¹, regardless of the attacking species, with reverse barriers (ΔE_2^\ddagger) of 19.1 (Me), 13.5 (Et) and 12.8 (*i*-Pr) kJ mol⁻¹. The trends in ΔE_2^\ddagger are as expected on the basis of leaving radical stability (*i*-Pr > Et > Me). Similar trends in ΔE_1^\ddagger and ΔE_2^\ddagger are observed at the QCISD/DZP//MP2/DZP level of theory.

Analogous calculations involving germlytellurol (H₃GeTeH) reveal energy barriers for the forward and reverse reactions which are much more similar in magnitude than the previously presented silicon data. MP2/DZP calculations predict barriers (ΔE_1^\ddagger) of 30.7, 30.0 and 26.0 kJ mol⁻¹ for the reactions of methyl, ethyl and *iso*-propyl radicals respectively at tellurium with expulsion of GeH₃, while the reverse reactions are predicted to proceed with barriers of 29.0, 23.2 and 20.2 kJ mol⁻¹ respectively. Differences of only 1.7 to 6.8 kJ mol⁻¹ in the forward and reverse barriers would be expected to manifest themselves as equilibria, with equilibrium constants (K_E) of between approximately 0.6 and 0.1 at 80°C, assuming similar entropy terms. These data, combined with the MP2/DZP calculated activation energies (20–31 kJ mol⁻¹) and the knowledge that many effective chain-carrying radical reactions proceed with barriers of less than approximately 30 kJ mol⁻¹ [12] suggest that reactions involving trialkylgermyl radicals at alkyltellurides with the formation of alkyl radicals are indeed reversible and are consistent with our NMR studies detailed above. Interestingly, the QCISD/MP2 (single point) calculations predict these reactions to be essentially irreversible ($K_E \sim 10^{-4}$) and are not consistent with the available

experimental (NMR) data. Once again, differences in the MP2/DZP and QCISD/DZP generated potential energy surfaces are most likely to be responsible for the significant divergence between MP2 and QCISD (single point) data.

Inspection of Table 1 reveals that in all cases in this study, MP2/DZP calculations predict that alkyl radical attack at tellurium with expulsion of SnH₃ is exothermic, with forward barriers (ΔE_1^\ddagger) of 28.8 (Me), 26.8 (Et) and 22.4 (*i*-Pr) kJ mol⁻¹. The analogous reverse barriers (ΔE_2^\ddagger) are predicted to be 40.3 (Me), 33.2 (Et) and 29.8 (*i*-Pr) kJ mol⁻¹. Similar considerations to those applied to the analogous reactions involving germly radical leads to predicted equilibrium constants (K_E) of approximately 50 (Me), 10 (Et) and 12 (*i*-Pr). Clearly then, alkyl radicals in general are predicted to be capable of displacing stannyl radicals from tellurium, once again, in agreement with the previously presented experimental (NMR) data.

It is interesting to note that tris(trisilyl)silyl radicals are calculated to react exothermically with methyltellurol; MP2/DZP calculations predict ΔE_2^\ddagger to be 16.1 kJ mol⁻¹, with the barrier for methyl radical attack (ΔE_1^\ddagger) predicted to be 29.9 kJ mol⁻¹. Similar data are provided by the single-point QCISD data. We have previously reported that the silyl group is a poor model for the trimethylsilyl group in ab initio calculations involving substituted carbenium ions; [64] it is highly likely that Si(SiH₃)₃ also performs poorly as a model for Si(SiMe₃)₃ in this study.

2.6. Equilibria in radical reactions

Because of the nature of many free-radical reactions which rely on the establishment of chain mechanisms (e.g., Scheme 2), it is unlikely that true equilibria can ever be established because of competing chain-propagating steps. Consequently, the NMR data presented in

Table 2
SCF/DZP, MP2/DZP and QCISD/DZP^a calculated energies^b of the reactants, products and transition states in this study

Structure	SCF	MP2	QCISD/MP2 ^a
Me ·	−39.57176 ^{c,d}	−39.69727 ^{c,d}	−39.71891 ^{c,d}
Et ·	−78.61706 ^c	−78.88130 ^c	−78.91699 ^c
<i>i</i> -Pr ·	−117.66350 ^c	−118.06814 ^c	−118.11713 ^c
·SiH ₃	−5.46984 ^d	−5.55964 ^d	−5.58357 ^d
·GeH ₃	−5.34597 ^d	−5.43346 ^d	−5.45694 ^d
·SnH ₃	−4.94363 ^{c,d}	−5.02396 ^{c,d}	−5.04697 ^{c,d}
·Si(SiH ₃) ₃	−20.31222	−20.69008	−20.77086
MeTeH	−48.04744 ^d	−48.29930 ^d	−48.33181 ^d
EtTeH	−87.08781	−87.48223	−87.52711
¹ PrTeH	−126.13002	−126.66945	−126.72578
H ₃ SiTeH	−13.96715 ^d	−14.17021 ^d	−14.20770 ^d
H ₃ GeTeH	−13.83733 ^d	−14.03700 ^d	−14.07400 ^d
H ₃ SnTeH	−13.43211 ^d	−13.62247 ^d	−13.65911 ^d
(H ₃ Si) ₃ SiTeH	−28.80051	−29.29736	−29.38810
MeTe(H)SiH ₃	−53.50337 ^d	−53.85230 ^d	−53.91172 ^d
MeTe(H)GeH ₃	−53.37852 ^d	−53.72171 ^d	−53.78117 ^d
MeTe(H)SnH ₃	−52.97540 ^d	−53.80792 ^d	−53.36730 ^d
EtTe(H)SiH ₃ ([19])	−92.54590	−93.03601	−93.10713
EtTe(H)GeH ₃ ([20])	−92.42140	−92.90687	−92.97881
EtTe(H)SnH ₃ ([21])	−92.01846	−92.49354	−92.56548
¹ PrTe(H)SiH ₃ ([22])	−131.58919	−132.22418	−132.30611
¹ PrTe(H)GeH ₃ ([23])	−131.46464	−132.09522	−132.17866
¹ PrTe(H)SnH ₃ ([24])	−131.06187	−131.68208	−131.76572
MeTe(H)Si(SiH ₃) ₃ ([25])	−68.34303	−68.98324	−69.09634

^aQCISD/DZP/MP2/DZP.

^bEnergies in Hartrees ($1 E_h = 2626 \text{ kJmol}^{-1}$).

^c[61,63].

^d[37,38].

this paper serve only to establish that both the forward and reverse reactions as presented in Schemes 2 and 3 are occurring; the determination of equilibrium constant data from these NMR experiments is a highly unlikely outcome.

The calculated value of 22.4 kJ mol^{-1} for ΔE_1^\ddagger in the reaction of *iso*-propyl radical with stannyltelluride is likely to represent an upper limit for the activation energy for the reaction of *iso*-propyl radical with aryltellurotributyltin (**1**, **2**). Given that a value of 9 represents a reasonable estimate for the $\log[A/M^{-1} \text{ s}^{-1}]$ term in the Arrhenius expression for intermolecular homolytic substitution at a heavy main-group heteroatom,² [65] the rate constant for homolytic displacement of tributylstannyl radical from **1** by *iso*-propyl radical can be estimated to be greater than $4.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 80°C . The rate constant for hydrogen abstraction by secondary alkyl radicals from tributyltin hydride is well established to be $3.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at 80°C . [19,65] As the reactions in question (Scheme 3) are carried out in the presence of 5 mol% tributyltin hydride, the *iso*-propyl radical can be estimated to react more than approximately 3 times more effectively with **1** than with

tributyltin hydride; it is therefore not surprising that alkyldestannylation at tellurium is competitive with hydrogen abstraction from tributyltin hydride under the reaction conditions described.

Similar considerations when applied to the reaction of methyl radical at the selenium atom in **15**, with an approximate activation energy of 50 kJ mol^{-1} [37,38] and $\log[A/M^{-1} \text{ s}^{-1}]$ estimate of 9 leads to approximate relative reaction rates of 2×10^{-4} and 1.0 for attack of methyl radical at **15** and tributyltin hydride respectively under the described reaction conditions. With this in mind, it is not surprising that methyl radical failed to displace the tributylstannyl radical from the arylselenotributyltin species (**17**, **18**); abstraction of hydrogen atom from the tributylstannane present would be expected to be the favoured process.

2.7. Conclusion

²⁹Si, ¹¹⁹Sn and ¹²⁵Te NMR spectroscopy together with ab initio molecular orbital calculations confirm that under standard radical conditions, alkyl radicals are capable of displacing tributylstannyl, tributylgermyl and tris(trimethylsilyl)silyl radicals from the tellurium atom in alkyl tellurides.

Consequently, reactions involving aryltellurides as radical precursors together with chain carrying species

² Based on the reaction of 1-octyl radical with iodocyclohexane. [65]

such as tributyltin hydride, tributylgermanium hydride and tris(trimethylsilyl)silane may involve reversible homolytic substitution at tellurium leading to reduced reactions yields.

3. Experimental

Tris(trimethylsilyl)silane was purchased from Fluka, tellurium powder was purchased from Aldrich and tributylgermanium chloride was a gift.³ Tributylgermanium hydride and tributyltin hydride were prepared following literature procedures [66,67]. Compounds **3–8**, **17**, **18** were prepared according to previously published procedures [40,42,43,68].

[(4-Fluorophenyl)telluro]ethane (**7**) was prepared following Standard Protocol (E) in our previously published procedure [40] using bis(4-fluorophenyl) ditelluride and iodoethane. Kügelrohr distillation (45°C/0.08 mm) afforded **7** as a yellow oil (70%). ¹H NMR (CDCl₃): δ 1.37 (t, 3H, *J* = 7.5 Hz); 2.45 (q, 2H, *J* = 7.5 Hz); 6.59 (m, 2H); 7.42 (m). ¹³C NMR (C₆D₆): δ 0.6; 17.4; 105.5 (*J*_{C–F} = 3.5 Hz); 116.6 [*J*(¹³C–¹⁹F) = 20.8 Hz]; 141.3 [*J*(¹³C–¹⁹F) = 7.1 Hz] 163.2 [*J*(¹³C–¹⁹F) = 246.8 Hz]. ¹²⁵Te NMR: δ 551.2. MS *m/e* 254 (30%, M⁺); 225 (29%); 130 (25%); 95 (100%). HRMS: C₈H₉FTe requires 253.9758; found 253.9763.

2-[(4-Fluorophenyl)telluro]butane (**9**) was prepared following Standard Protocol (E) in our previously published procedure [40] using bis(4-fluorophenyl) ditelluride and 2-iodobutane. Kügelrohr distillation (50°C/0.08 mm) afforded **9** as a yellow oil (70%). ¹H NMR (CDCl₃): δ 0.97 (t, 3H, *J* = 7.1 Hz); 1.57–1.74 (m, 5H); 3.34 (q, 1H, *J* = 7.1 Hz); 6.91 (m, 2H); 7.75 (m, 2H). ¹³C NMR (C₆D₆): δ 13.9; 23.9; 26.3; 32.4; 105.5 [*J*(¹³C–¹⁹F) = 3.6 Hz]; 116.4 [*J*(¹³C–¹⁹F) = 20.4 Hz]; 142.6 [*J*(¹³C–¹⁹F) = 7.7 Hz]; 162.9 [*J*(¹³C–¹⁹F) = 247.8 Hz]. ¹²⁵Te NMR: δ 645.8. MS *m/e* 282 (3%, M⁺); 225 (16%); 130 (12%), 95 (68%); 91 (100%). HRMS: C₁₀H₁₃FTe requires 280.0064; found 280.0060.

3.1. General procedure for the in situ preparation of selenostannanes (1, 2), selenogermanes (10, 11) and selenosilanes (13, 14). Preparation of phenyltellurotributylstannane (1)

Tributyltin hydride (94 μl, 0.35 mmol) and AIBN (5 mol%) was added to a solution of phenyltellurocyclohexane (**3**, Ar = Ph) (100 mg, 0.35 mmol) in C₆D₆ (0.5 ml) in an NMR tube. The solution was heated at 80°C for 2 h while shielded from background light. The

colourless solution was examined by ¹H, ¹³C, ¹¹⁹Sn and ¹²⁵Te NMR spectroscopy which revealed the absence of starting materials and the in situ formation of **1** together with cyclohexane as the only products of reaction.

¹H NMR: δ 0.85 (t, 9H, *J* = 7.5 Hz); 1.09–1.14 (m, 6H); 1.20–1.31 (m, 6H); 1.41 (s, cyclohexane); 1.44–1.55 (m, 6H); 6.85 (t, 2H, *J* = 7.5 Hz); 7.00 (t, 1H, *J* = 7.1 Hz); 7.85 (dd, 2H, *J* = 7.2, 1.2 Hz). ¹³C NMR: δ 13.5 [*J*(¹³C–¹¹⁹Sn) = 296.6 Hz, *J*(¹³C–¹¹⁷Sn) = 283.0 Hz]; 13.9; 27.3 [*J*(¹³C–¹¹⁹Sn) = 56.6 Hz]; 27.3 (cyclohexane); 29.9 [*J*(¹³C–¹¹⁹Sn) = 21.9 Hz]; 103.5; 125.2; 129.0; 142.2. ¹¹⁹Sn NMR: δ –1.3 [*J*(¹¹⁹Sn–¹²⁵Te) = 2693 Hz, ¹*J*(¹¹⁹Sn–¹³C) = 299.1 Hz]; ¹²⁵Te NMR: δ –209.4 [*J*(¹²⁵Te–¹¹⁹Sn) = 2693 Hz, *J*(¹²⁵Te–¹¹⁷Sn) = 2578 Hz].

3.2. (4-fluorophenyl)tellurotributylstannane (2)

The title compound was prepared according to the general procedure using (4-fluorophenyl)tellurocyclohexane.

¹H NMR: δ 0.87 (t, 9H, *J* = 7.5 Hz); 1.09–1.14 (m, 6H); 1.20–1.31 (m, 6H); 1.41 (s, cyclohexane); 1.44–1.55 (m, 6H); 6.58 (m, 2H); 7.27 (m, 2H). ¹³C NMR: δ 13.8 [*J*(¹³C–¹¹⁹Sn) = 296.6 Hz, *J*(¹³C–¹¹⁷Sn) = 283.0 Hz]; 27.3 (cyclohexane); 27.4 [*J*(¹³C–¹¹⁹Sn) = 63.7 Hz]; 30.0 [*J*(¹³C–¹¹⁹Sn) = 21.9 Hz]; 105.6 [*J*(¹³C–¹⁹F) = 4.1 Hz]; 116.5 [*J*(¹³C–¹⁹F) = 15.8 Hz]; 144.0 [*J*(¹³C–¹⁹F) = 7.6 Hz]; 164.5 [*J*(¹³C–¹⁹F) = 247.8 Hz]. ¹¹⁹Sn NMR δ 0.4 [*J*(¹¹⁹Sn–¹²⁵Te) = 2656 Hz]. ¹²⁵Te NMR δ –213.9 [*J*(¹²⁵Te–¹¹⁹Sn) = 2656 Hz, *J*(¹²⁵Te–¹¹⁷Sn) = 2526 Hz].

3.3. Phenyltellurotributylgermane (10)

The title compound was prepared according to the general procedure using tributylgermanium hydride and AIBN (15 mol%) with heating at 80°C for 4 h.

¹H NMR: δ 0.80 (t, 9H, *J* = 7.5 Hz); 0.98–1.04 (m, 6H); 1.18–1.35 (m, 6H); 1.41 (s, cyclohexane); 1.35–1.40 (m, 6H); 6.78 (t, 2H, *J* = 7.5 Hz); 6.94 (t, 1H, *J* = 7.5 Hz); 7.85 (dd, 2H, *J* = 7.2, 1.2 Hz). ¹³C NMR: δ 13.9; 16.6; 26.5; 27.3 (cyclohexane); 27.7; 114.0; 126.9; 128.8; 142.1. ¹²⁵Te NMR δ –78.8.

3.4. (4-fluorophenyl)tellurotributylgermane (11)

The title compound was prepared according to the general procedure using (4-fluorophenyl)tellurocyclohexane, AIBN (15 mol%) and tributylgermanium hydride with heating at 80°C for 4 h. ¹H NMR: δ 0.89 (t, 9H, *J* = 7.5 Hz); 1.03–1.09 (m, 6H); 1.20–1.35 (m, 6H); 1.41 (s, cyclohexane); 1.39–1.45 (m, 6H); 6.59 (m, 2H); 7.53 (m, 2H). ¹³C NMR: δ 13.3; 17.1; 26.3; 27.3 (cyclohexane); 28.5; 96.2; 116.3 [*J*(¹³C–¹⁹F) =

³ We thank Professor D. Dakternieks for providing a sample of tributylgermanium chloride.

20.6 Hz]; 143.8 [$J(^{13}\text{C}-^{19}\text{F}) = 7.5\text{ Hz}$]; 163.5 [$J(^{13}\text{C}-^{19}\text{F}) = 248.3\text{ Hz}$]. ^{125}Te NMR δ -82.8.

3.5. Phenyltellurotris(trimethylsilyl)silane (13)

The title compound was prepared according to the general procedure using tris(trimethylsilyl)silane.

^1H NMR: δ 0.26 (s, 27H); 1.41 (cyclohexane); 6.81 (t, 2H, $J = 7.5\text{ Hz}$); 7.00 (t, 1H, $J = 7.5\text{ Hz}$); 7.82 (dd, 2H, $J = 6.7, 1.5\text{ Hz}$). ^{13}C NMR: δ 1.54 [$J(^{13}\text{C}-^{29}\text{Si}) = 53.6\text{ Hz}$]; 27.3 (cyclohexane); 104.4; 127.7; 129.0; 142.3. ^{29}Si NMR δ -94.4; 10.6. ^{125}Te NMR δ -192.9.

3.6. (4-fluorophenyl)tellurotris(trimethylsilyl)silane (14)

The title compound was prepared according to the general procedure using (4-fluorophenyl)tellurocyclohexane and tris(trimethylsilyl)silane.

^1H NMR: δ 0.19 (s, 27H); 1.41 (cyclohexane); 6.87 (m, 2H); 7.73 (m, 2H). ^{13}C NMR: δ 2.01 [$J(^{13}\text{C}-^{29}\text{Si}) = 47.1\text{ Hz}$]; 27.3 (cyclohexane); 105.6 [$J(^{13}\text{C}-^{19}\text{F}) = 4.1\text{ Hz}$]; 116.6 [$J(^{13}\text{C}-^{19}\text{F}) = 20.4\text{ Hz}$]; 143.0 [$J(^{13}\text{C}-^{19}\text{F}) = 7.6\text{ Hz}$]; 165.0 [$J(^{13}\text{C}-^{19}\text{F}) = 247.9\text{ Hz}$]. ^{29}Si NMR δ -92.6 [$J(^{29}\text{Si}-^{125}\text{Te}) = 135\text{ Hz}$]; 10.6. ^{125}Te NMR δ -195.9.

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