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Synthesis and some reactivity studies of germanium, tin and lead analogues of alkynes†

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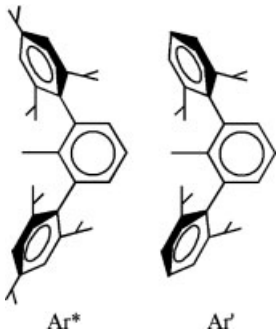
Recently published work on the syntheses and reactivity of the germanium, tin, and lead analogues of alkynes is summarized. The heavier Group 14 'alkynes' are stabilized by bulky terphenyl ligands and are thermally robust crystalline solids. However, they are extremely reactive and their reactivity decreases in the order Ge > Sn > Pb. Their spectroscopy and reactivity patterns suggest that the germanium species, in particular, has considerable diradical character. This hypothesis is also supported by preliminary density functional theory calculations. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: germanium; tin; lead; multiple bond; terphenyl; diradicaloid

INTRODUCTION

The recently synthesized germanium, tin and lead analogues of alkynes (ArEEAr, E = Ge, Sn, or Pb; Ar = terphenyl) display unique structural, spectroscopic and reactivity patterns. The compounds were first reported as stable species in 2000,[1] although, beginning in 1997, their reduced uninegative[2] and dinegative anions[3] were described in a number of papers.[4] The stabilization of the compounds was effected by use of the large terphenyl[5] substituents Ar* and Ar′.



These ligands can be synthesized in >100 g quantities as their iodide derivatives in a one-pot synthesis.[6,7] The iodides can be converted quantitatively to their lithium salts by treatment with ^{n}BuLi.[8] The lithium salts can then be used as transfer agents to synthesize the divalent arylelement(II) halide derivatives as shown in Eqn (1):[9,10]

$$ArLi + EX_2 \longrightarrow ArEX + LiX \quad (1)$$

(Ar = Ar′ or Ar*; E = Ge, Sn or Pb; X = Cl or Br)

Reduction of the aryl germanium or tin halide with sodium or potassium in various stoichiometries affords the neutral or reduced species as shown in Eqn (2).[1–4] These reductions occur so readily that the mono-[2] and di-anion[3] species were isolated before their neutral counterparts.

$$2ArEx + nM \longrightarrow ArEEAr, M\{ArEEAr\} \text{ or } M_2\{ArEEAr\} + 2MX \quad (2)$$

(Ar = Ar′ or Ar*; E = Ge or Sn; M = Li, Na or K; n = 2, 3 or 4)

In contrast, the neutral lead analogue Ar*PbPbAr*[1] was synthesized by treatment of Ar*PbBr with $LiAlH_4$ or $^{i}Bu_2AlH$:

$$LiAlH_4 + 2Ar^*PbBr \longrightarrow Ar^*PbPbAr^* + \text{other products} \quad (3)$$

No reduced Ar*PbPbAr* species, i.e. [Ar*PbPbAr*]$^-$ or [Ar*PbPbAr*]$^{2-}$, have been isolated to date.

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STRUCTURES AND SPECTROSCOPY

The structural data for the neutral and reduced germanium and tin species are summarized in Fig. 1. The structures of the neutral species show that the C(ipso)EEC(ipso) array has a planar, trans-bent arrangement (local symmetry C_{2h}) instead of the linear geometry usually found in alkynes. The bent structure arises from mixing of a low-lying σ^* and the in-plane π orbital in C_{2h} symmetry to afford an n_- combination (Fig. 2).[4] In this way, the bond order is decreased from three to near two in the trans-bent structure. The Ge–Ge and Sn–Sn bond distances are consistent with double bonding and are shorter than single Ge–Ge (2.44 Å) and Sn–Sn (2.81 Å) bonds, but are not as short as those calculated for a triply bonded linear structure.[12–14] In fact, the linear geometries do not represent minima on the potential surfaces and, although the calculated bond energies are shorter than those in the bent geometries, they are less stable by as much as 40 kcal mol^{-1} than the trans-bent structures.

The structure of the lead species differs from those of germanium or tin because the trans-bending angle is almost 90°.[1] Moreover, the lead–lead bond, at 3.188(1) Å, is significantly longer than the *ca* 2.9 Å normally found in organometallic lead–lead-bonded species, such as $Me_3PbPbMe_3$. The structure is best viewed according to the drawing in Fig. 3, in which there are lone pairs that are mainly 6s in character at each lead and there is a long lead–lead single σ bond derived from head-to-head overlap of 6p orbitals.

Inspection of the structural data in Fig. 1 affords further insight into the electronic structure of the neutral germanium and tin species. The germanium and tin compounds are readily reduced at −1.38 and −1.21 V (versus saturated calomel electrode (SCE)) to afford the monoanions.[11] Stirring

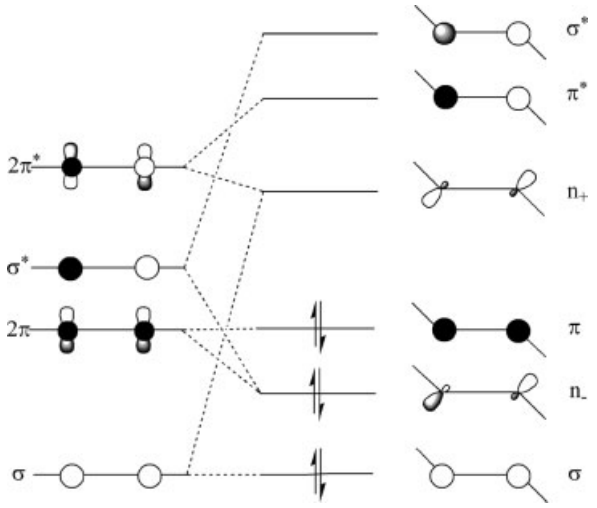


Figure 2. Schematic drawing illustrating the mixing of the σ^* and π level that occurs upon trans-bending of the CEEC (E = Si–Pb) geometry.

the compounds for longer periods affords doubly reduced salts. For the germanium compound, the addition of one electron results in a small (0.024 Å) increase in the Ge–Ge bond length and a *ca* 14° decrease in the bending angle. These changes suggest that the electron has entered an orbital that is mostly non-bonding in character. This is consistent with Fig. 2, where the lowest unoccupied molecular orbital (LUMO) is depicted as the n_+ lone pair combination, which is non-bonding. Addition of another electron to give the dianion results in a larger bond length increase (0.085 Å) and a further narrowing of *ca* 12.5° of the bending angle. The

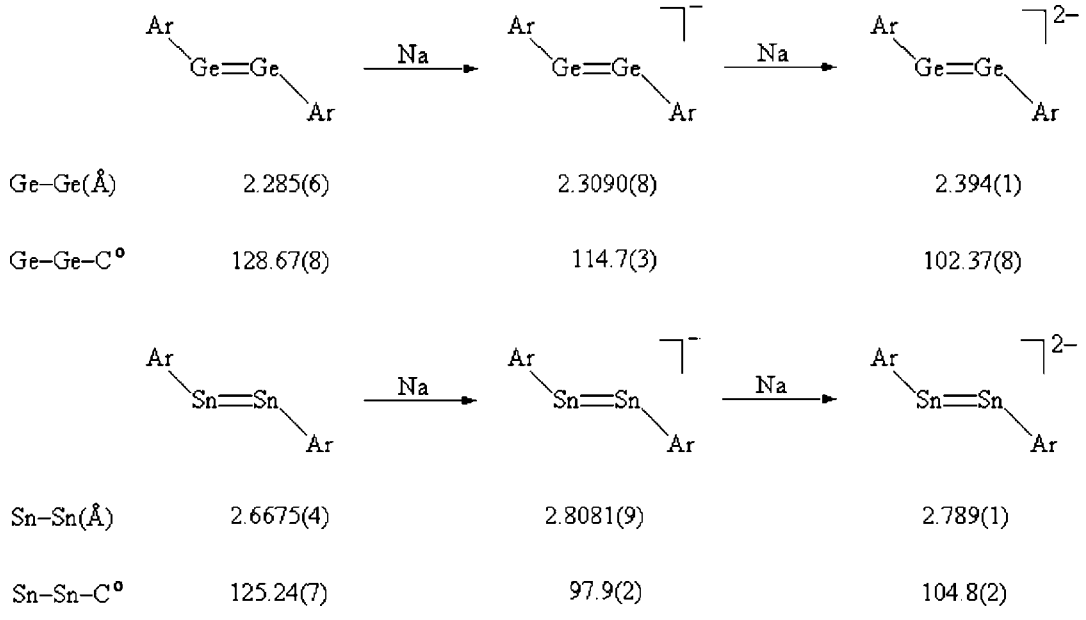


Figure 1. Selected structural data for neutral and singly or doubly reduced digermynes and distannynes (Ar = Ar′ or Ar*[11]).

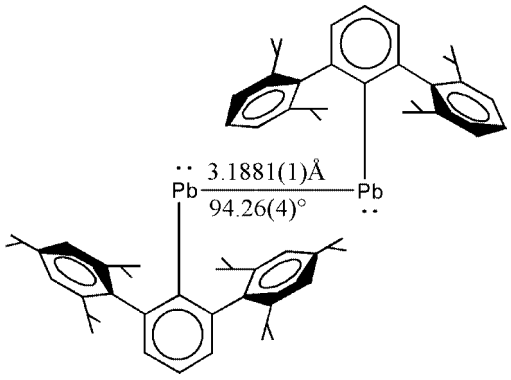


Figure 3. Important structural parameters from Ar*PbPbAr*.[1].

increase in the Ge–Ge bond length is probably the result of an increase in interelectronic repulsion that occurs on formation of the dianion rather than a significant change in the orbital character to antibonding. The proportionate narrowing of the bending angle upon the addition of one or two electrons is also consistent with these electrons residing in a non-bonding orbital that is mainly lone pair character (i.e. n_+).

The structural trends in the reduction of the tin compound are not as easily explained, because there is a substantial (0.14 Å) increase in the Sn–Sn bond length upon addition of one electron that is accompanied by a very sharp (27.3°) narrowing of the bending angle to 97.9(2)°. It is possible that the changes in the character of the σ bonding that occur with this large increase in bending could account for some of this increase. Oddly, the addition of a further electron, to give the dianion, results in a *ca* 0.02 Å shortening of the bond and a widening of the bending angle to 104.8(2)°. It is notable, however, that the bending angles in the germanium and tin dianions are very similar and that the Ge–Ge and Sn–Sn distances are significantly shorter than single bonds. It should be realized that the dianions are isoelectronic to the corresponding neutral Group 15 ArAsAsAr and ArSbSbAr species[15] and the Ge–Ge and Sn–Sn bonds are properly regarded as double bonds. Unfortunately, no reduction products of the lead species Ar*PbPbAr* are available for comparison. It seems likely that the addition of electrons to this compound will afford significantly shorter Pb–Pb bonds and perhaps wider bending angles.

Table 1. Electronic spectral data and reduction potentials for Ar′EEAr′ (E = Ge or Sn) and Ar*PbPbAr*[11]

Compound	UV–Vis λ (nm) [ε (M^{-1} L cm^{-1})]		Reduction wave (V)
Ar′GeGeAr′	500 [7500]	371 [34 000]	−1.39[a]
ArSnSnAr′	597 [1700]	410 [3400]	−1.21[a]
Ar*PbPbAr*	750 [5200]	397 [29 000]	−1.71[b]

[a] vs SCE.
[b] vs Ag/Ag^+.

The neutral germanium (carmine red), tin (dark blue–green) and lead (dichroic olive green–orange) compounds are characterized by intense colors.[11] This is consistent with their UV–visible spectra (Table 1), in which two absorptions are observed in *n*-hexane solution.

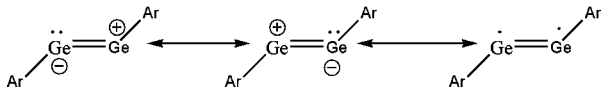
The intensity of the absorptions suggests they are both orbitally allowed. Since it is known that the highest occupied molecular orbital (HOMO) is a π orbital, the LUMO has considerable n_+ character, and the LUMO + 1 is π^*, it seems likely that the absorptions are due to $\pi \rightarrow n_+$ and $\pi \rightarrow \pi^*$ transitions, both of which are orbitally allowed. The higher energy absorption can be tentatively assigned to $\pi - \pi^*$ (involving the orbitals perpendicular to the molecular plane) with the lower energy absorption assigned to $\pi \rightarrow n_+$ transition.

The germanium, tin and lead compounds afford what appear to be normal ^1H and ^{13}C NMR spectra. Attempts to obtain ^{119}Sn and ^{207}Pb NMR spectra, however, have not been successful so far, despite numerous attempts to record them. It is conceivable that failure to detect signals could be due to very unusual shifts. It is also possible that the unsymmetric environments at tin or lead could cause very anisotropic chemical shift tensors that could result in sufficient broadening of the signals to make them undetectable under ambient conditions. However, it is notable that related organoderivatives such as Sn(Ph)Ar*[16] or Pb(Me)Ar*[9] readily afford signals for the ^{119}Sn and ^{207}Pb nuclei. Another possibility is that there are low-lying paramagnetic excited states that cause unusual chemical shifts and signal broadening that render detection difficult. The latter explanation for the failure to detect the signals is also consistent with the possible diradical character suggested below.

REACTIONS OF THE HEAVIER GROUP 14 ALKYNE ANALOGUES

The facile reductions of the neutral germanium or tin alkynes are indicative of low-lying energy levels within the molecule and suggest a high reactivity. The compounds are exceedingly air and moisture sensitive, but the products that arise from their direct reaction with O_2 or H_2O have not been fully analyzed. The first reaction product to be isolated and characterized arose from the treatment of Ar*GeGeAr* with 2,3-dimethyl-1,3-butadiene. In this case, it was expected that a simple cyclic product arising from a 2 + 4 addition of the Ge≡Ge triple bond to the diene would be obtained. Instead, the product illustrated in Figure 4 was crystallized thus.[17]

This product is unusual, in that it could be interpreted in terms of the existence of an exceedingly reactive diradical character in germanium species, as shown by the latter canonical form.



Thus, the reaction of each radical center could give rise to the two five-membered GeC_4 rings. Steric congestion could then

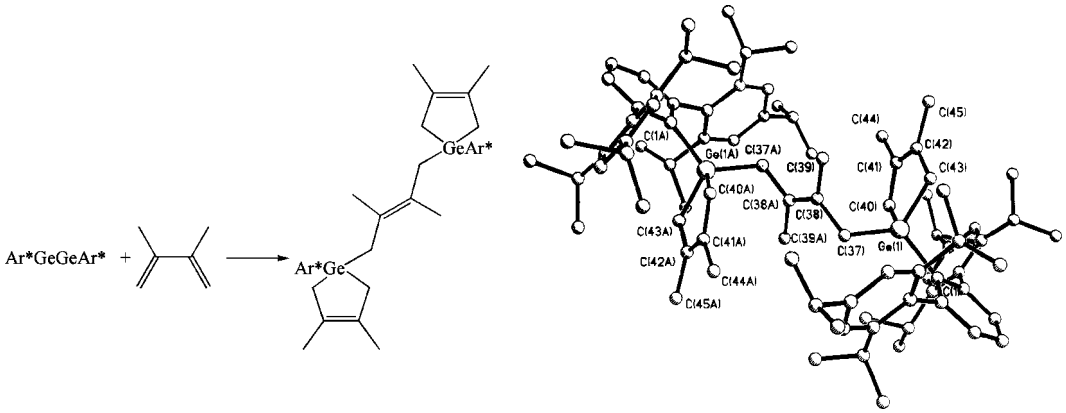


Figure 4. Reaction of Ar*GeGeAr* with 2,3-dimethyl-1,3-butadiene.[17]

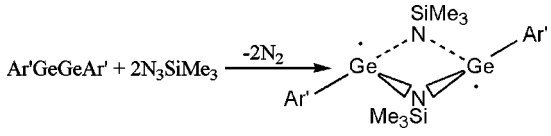
Si	Ge	Sn	Pb
Triplet 18.3	Triplet 15.8	Singlet 6.8	Singlet 11.9
Singlet Real minimum 11.9	Triplet 7.9	Triplet 5.7	Singlet Real minimum 6.9
Triplet 9.6	Singlet Real minimum 6.1	Triplet 1.4	Triplet 3.8
Singlet 7.9	Singlet Real minimum 5.8	Singlet Real minimum 0.8	Triplet 1.8
Singlet Real minimum 0.0	Singlet Real minimum 0.0	Singlet Real minimum 0.0	Singlet Real minimum 0.0

Figure 5. Relative energies (kcal mol^{-1}) of geometric isomers of MeEEMe (E = Si–Pb) B3LYP/6-31G* for silicon and germanium (Brynda and Power, unpublished results).

cause homolytic cleavage of the Ge–Ge bond which could then add a further equivalent of the diene to give the product in Figure 4.

The view that the digermyne could have singlet diradical character receives support from DFT calculations (Fig. 5) which show that there are low-lying triplet states near the trans-bent singlet state. These low-lying triplet states are usually indicative of considerable singlet diradical character and high reactivity.

The digermene reacts readily with numerous small molecules, including H_2, N_2O, O_2, N_3SiMe_3, PhCCPh, Me_3SiCCH, PhNNPh, ^tBuNC, P_4, S_8 and others (see Fig. 6). Among the most interesting of these reactions is that with N_3SiMe_3,[18] which affords the ring product $Ar'Ge(\mu\text{-}NSiMe_3)_2GeAr'$:



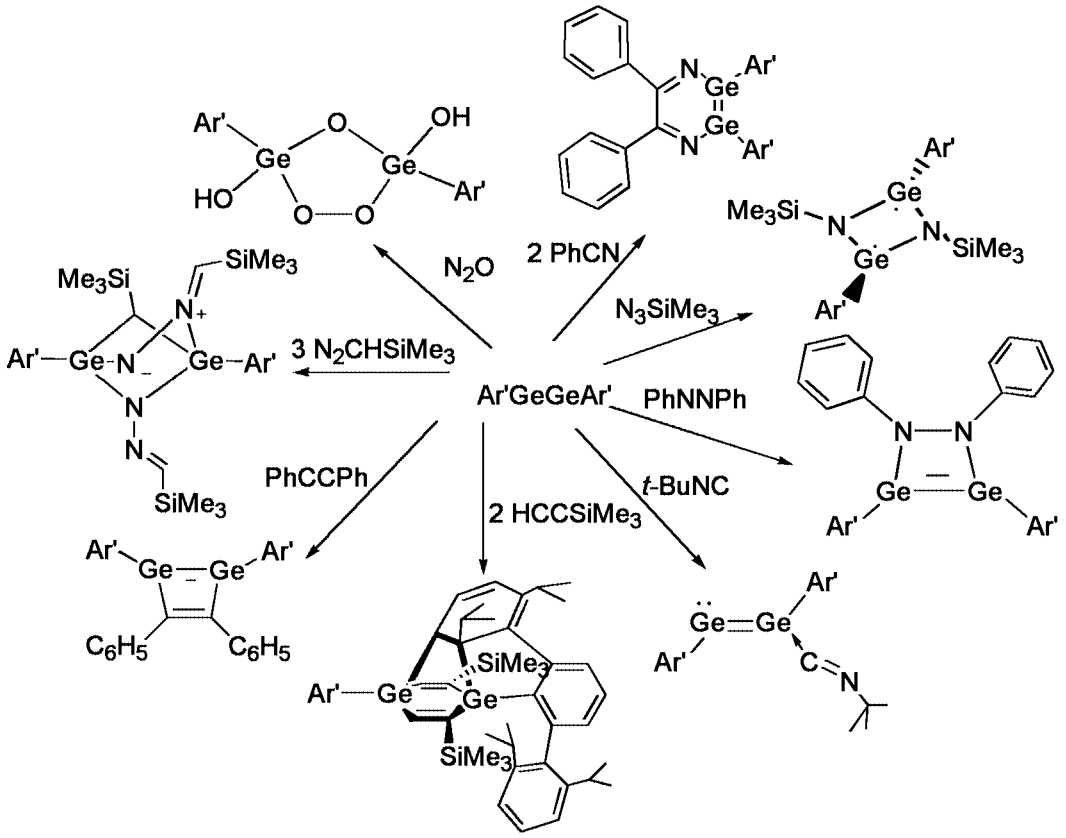


Figure 6. Reactions of Ar′GeGeAr′ with unsaturated molecules[18,19], (Gin and Power, unpublished results).

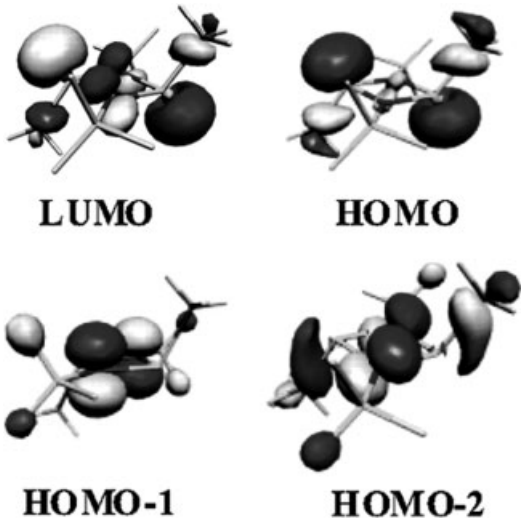
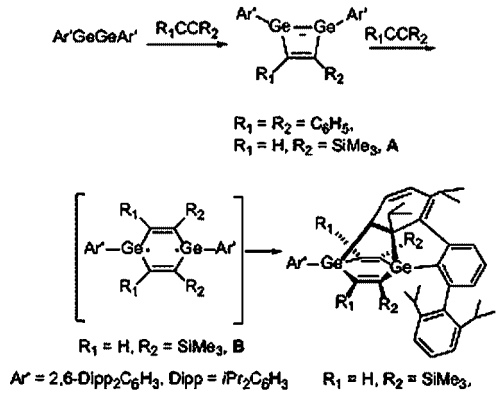


Figure 7. Frontier orbitals in Ar′Ge(μ-NSiMe$_3$)$_2$GeAr′.[18]

The cyclic Ge_2N_2 product is a highly reactive purple crystalline solid that attacks solvents such as benzene and reacts directly with hydrogen. Calculations show that there is a small (*ca* 17.5 kcal mol^{-1}) singlet–triplet gap consistent with singlet diradical character. The HOMO and the LUMO orbitals (Figure 7) are essentially non-bonding ones, and this is also consistent with their diradical character.

Other evidence for diradical character comes from the reaction of Ar′GeGeAr′ with PhCCPh or Me$_3$SiCCH, as shown in Eqn (5):[19]



Although, the reaction with PhCCPh proceeds normally to give a cyclic product, the use of the less bulky alkyne Me$_3$SiCCH results in a product involving an activated aryl ring of one of the flanking C_6H_3-2,6-^{i}Pr$_2$ rings of one of the terphenyls; this is believed to proceed by the diradical

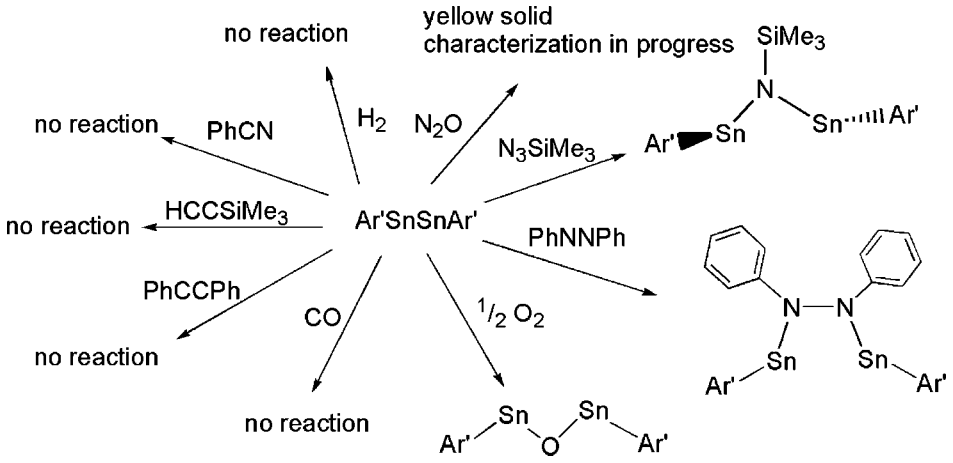


Figure 8. Reactions of Ar′SnSnAr′ with unsaturated molecules (Gin and Power, unpublished results).

intermediate B, which is sufficiently reactive to induce the aryl ring activation.

As discussed above, the high degree of reactivity of the Ar′GeGeAr′ or Ar*GeGeAr* species receives support from density functional theory (DFT) calculations on the model methyl-substituted species (Figure 5). These show that, for MeEEMe (E = Si–Pb), there is no instance in which a triplet species lies more than a 10 kcal mol^{-1} from the real minimum. The calculations also indicate that only in the case of germanium is a trans-bent structure resembling that found for Ar′GeGeAr′ found to be minimum on the potential surface. In the case of the silicon, tin, and lead derivatives, the singlet trans-bent structure is, in effect, an intermediate that is stabilized (at least in the case of tin and lead) by the bulky terphenyl ligand. The DFT calculations also suggest high reactivity for the silicon, tin and lead analogues of the germanium species. Initial investigations (Gin and Power, unpublished results) of the reactivity of the tin compounds Ar′SnSnAr′ and Ar*PbPbAr* show that they are not as reactive as the germanium analogue. For example, they undergo no reaction with Me_3SiCCH, PhCCPh or H_2 (Figure 8). An explanation for such differences will require further investigation, and details of all the reaction products of Ar′GeGeAr′ and Ar′SnSnAr′ will be given in future publications.

Acknowledgements

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