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Formation of $[\mathrm{Ar^*\overline{Ge\{CH_2C(Me)C(Me)C}H_2\}CH_2C(Me)\!=}]_2$ (Ar* = C_6H_3-2,6-$Trip_2$; Trip = C_6H_2-2,4,6-*i*-Pr_3) *via* reaction of Ar*GeGeAr* with 2,3-dimethyl-1,3-butadiene: evidence for the existence of a germanium analogue of an alkyne

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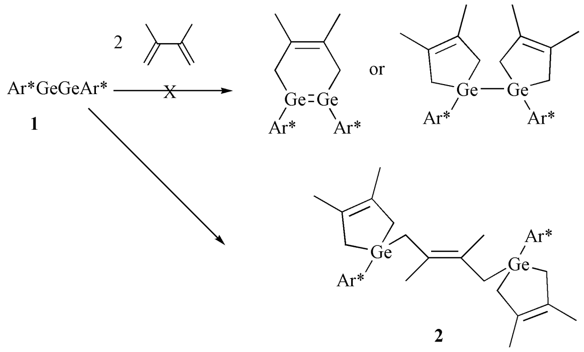
The reduction of Ar*GeCl (Ar* = C_6H_3-2,6-$Trip_2$; Trip = C_6H_2-2,4,6-*i*-Pr_3) with one equivalent of potassium leads to the formation of a germanium analogue of an alkyne Ar*GeGeAr* 1; reaction of 1 with 2,3-dimethyl-1,3-butadiene yields $[\mathrm{Ar^*\overline{Ge\{CH_2C(Me)C(Me)C}H_2\}CH_2C(Me)\!=}]_2$ 2, which was structurally characterized.

The synthesis and characterization of compounds with multiple bonds between heavier main group elements are of fundamental interest due to their unusual structures and bonding.[1] In particular, numerous alkene analogues of the heavier group 14 elements with the general formula $R_2E{=}ER_2$ (E = Si–Pb; R = bulky organic group) have been isolated and characterized.[2] The structure and bonding of these compounds are very different from the olefins $R_2C{=}CR_2$, and they usually have a *trans* pyramidal (C_{2h}) geometry and an E=E bond that is prone to dissociate in solution in the case of the Ge, Sn or Pb derivatives.[1,2] Much less is known about the heavier group 14 congeners of alkynes REER (E = Si–Pb), although theoretical studies on various hypothetical molecules REER (E = Si–Sn; R = H, alkyl, aryl, silyl) predict a planar, *trans*-bent (C_{2h}) structure for alkyl or aryl substituted species instead of the linear geometry of the alkynes.[3] A recent paper has described the synthesis and X-ray structure of Ar*PbPbAr* which is the only currently known stable heavier group 14 element analogue of an alkyne.[4] It has a planar *trans*-bent CPbPbC core (Pb–Pb–C 94.2°) and a long, single Pb–Pb bond (Pb–Pb 3.188 Å) that is in agreement with calculations on model species.[5] A number of reports have indicated the existence of REER species (E = Si or Ge) as reactive intermediates, but they have yet to be isolated as stable entities.[6] Here, the synthesis and spectroscopic characterization of Ar*GeGeAr*, **1** (Ar* = C_6H_3-2,6-$Trip_2$, Trip = C_6H_2-2,4,6-*i*-Pr_3), which is a stable Ge analogue of an alkyne are reported. Crystals of **1** suitable for X-ray crystallography have not yet been obtained. However, treatment of **1** with two equivalents of 2,3-dimethyl-1,3-butadiene afforded $[\mathrm{Ar^*\overline{Ge\{CH_2C(Me)C(Me)C}H_2\}CH_2C(Me)\!=}]_2$ **2**, which has an unusual structure, derived from the interaction of **1** with three equivalents of 2,3-dimethyl-1,3-butadiene.

Reduction of Ar*GeCl[7] with one equivalent of K in THF at ambient temperature for 24 h afforded a dark red solution. After suitable work-up and recrystallization from toluene, **1** was obtained as analytically pure, red microcrystals in moderate yield (*ca.* 35%). It is thermally stable to about 200 °C at which the color begins to darken. The existence of **1** was supported by ^1H and ^{13}C NMR spectroscopy and C,H analysis.† A cyclic voltammogram of **1** in THF–toluene displayed a quasi reversible reduction at *ca.* -1.46 V *vs.* SCE. Attempts to obtain X-ray quality crystals of the 'digermyne' **1** for a structure determination have not yet been successful in spite of the use of several different solvents and crystallization methods. Previous work has shown that the reduction of Ar*GeCl with excess Na or K in THF afforded the reduced species Na_2Ar*GeGeAr*, K_2Ar*GeGeAr* or the radical NaAr*GeGeAr*.[8,9] These reactions strongly suggest that **1** is generated initially and is subsequently reduced by excess alkali metal.

In order to derivatize **1**, a reaction was performed with a stoichiometric amount of 2,3-dimethyl-1,3-butadiene in toluene at room temperature (Scheme 1). This afforded the product **2** as colorless crystals that are thermally stable up to the melting point of *ca.* 250 °C. No Ge–C bond cleavage, which could have resulted in the loss of the coordinated olefin, was observed up to its melting point. Such retro reactions are known to occur with Ge compounds synthesized by the addition of butadienes to germylenes.[10] The X-ray crystal structure‡ (Fig. 1) shows that Ge has a distorted tetrahedral geometry (interligand angles 91.2–120.8°; av. 109.1°) and Ge–C bond distances that span the range 1.954(5)–1.986(4) Å (av. 1.973 Å). The separation of the two Ge centers in the molecule is 6.534(2) Å. The Ge–C bond distances within the germacyclopent-3-ene ring are 1.954(5) and 1.970(5) Å which are within the range (1.950–1.991 Å) of the Ge–C distances in published germacyclopent-3-ene com-



Scheme 1

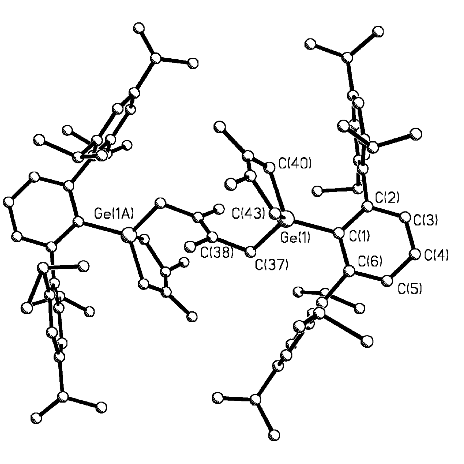


Fig. 1 Schematic drawing of **2**. H atoms are not shown. Selected bond distances (Å) and angles (°): Ge(1)–C(1) 1.986(4), Ge(1)–C(40) 1.970(5), Ge(1)–C(43) 1.954(5), Ge(1)–C(37) 1.982(4), C(37)–C(38) 1.507(6), C(38)–C(38A) 1.329(10), C(1)–C(2) 1.406(6), C(1)–C(6) 1.413(6); C(2)–C(1)–C(6) 117.9(4), Ge(1)–C(1)–C(43) 121.8(3), Ge(1)–C(1)–C(6) 119.8(3), C(40)–Ge(1)–C(43) 91.2(3), C(1)–Ge(1)–C(37) 114.2(2), C(1)–Ge(1)–C(40) 120.8(2), C(37)–Ge(1)–C(40) 107.2(2).

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pounds.[11,12] The angle at the Ge within the ring is 91.2(3)° which is also in good agreement with literature values [*ca.* 88–93°].[11,12] The five-membered ring incorporating the Ge atom shows a puckered C_s ring conformation. The degree of puckering, δ, of germacyclopent-3-enes is defined by the angle between the plane containing the four carbon atoms of the ring and that containing Ge and the two adjacent ring carbons. In the case of **2** the value for δ is 16.3° and the Ge atom shows an out of plane deviation of 0.3861 Å. The interplanar angle δ lies in the middle of the literature values which can vary between 6.0 and 30.2°. These angles depend on steric interactions of the other Ge substituents with the germacyclopent-3-ene ring which can have a large effect on δ since there is only a small difference in energy between the puckered (C_s) and planar (C_{2v}) ring conformation.[12] The formation of a 'bridged' product such as **2** on addition of a diene to germylenes was previously unknown. Initially, it was thought that a digermacyclohexadiene product would be obtained as illustrated in Scheme 1. However this involves a very sterically disfavored cis arrangement of Ar* groups which could weaken the Ge–Ge bond to such an extent that cleavage takes place to give a bis germylene species. This may add further butadiene to form **2**. Alternatively, since it is probable that **1** has a *trans* bent structure with lone pair electron density at each germanium, addition of butadiene could afford a cyclopentene moiety at each germanium. The resulting molecule could be so crowded that dissociation to give $\mathrm{Ar^*\overline{Ge\{CH_2C(Me)C(Me)CH}_2\}^{\bullet}}$ radicals could occur which could then add further 2,3-dimethyl-1,3-butadiene to yield **2**.

In summary a stable germanium analogue of an alkyne, **1**, has been isolated and characterized by NMR spectroscopy, elemental analysis and by its reaction with 2,3-dimethyl-1,3-butadiene to yield the unique product **2**.

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Notes and references

† All manipulations were carried out under anaerobic and anhydrous conditions. **1**: An orange solution of 1.68 g (2.85 mmol) of Ar*GeCl[7] in THF (30 ml) was added to 0.112 g (2.85 mmol) of finely divided potassium in THF (30 ml) at ambient temperature under vigorous stirring. After *ca.* 2 h the reaction mixture began to turn red, and upon stirring for further 24 h the solution had become deep red. The volatile materials were removed under reduced pressure and the red solid residue was extracted with hexane (50 ml). The remaining potassium chloride was allowed to settle and the supernatant solution was decanted off. The deep red solution was then concentrated to incipient crystallization (*ca.* 30 ml). Storage at 5 °C for 12 h yielded Ar*GeGeAr* **1**, as red microcrystals. Yield (M = 1108.92): 0.55 g, 0.49 mmol, 35%, mp 244–246 °C (darkens above 200 °C; stays glassy after melting and cooling). ^{1}H NMR (C_6D_6): δ 7.21–6.90 (m, 14H, *m*-Trip and *m*- and *p*-C_6H_3), 2.95 (sept, 4H, *p*-C*H*(CH_3)$_2$, ^3J 6.8 Hz), 2.75 (sept, 4H, *o*-C*H*(CH_3)$_2$, ^3J 6.8 Hz), 1.38 (d, 12H, *o*-CH(C*H*$_3$)$_2$, ^3J 7.2 Hz), 1.30 (d, 12H, *o*-CH(C*H*$_3$)$_2$, ^3J 7.2 Hz), 1.09 (d, 12H, *p*-CH(C*H*$_3$)$_2$, ^3J 7.2 Hz); ^{13}C NMR (C_6D_6): δ 156.8 (*i*-C_6H_3), 148.6 (*o*-C_6H_3), 146.1 (*o*-Trip), 139.1 (*p*-Trip), 128.6 (*i*-Trip), 128.2 (*m*-C_6H_3), 127.5 (*p*-C_6H_3), 121.7 (*m*-Trip), 34.6 (*p*-*C*H(CH_3)$_2$), 31.3 (*o*-*C*H(CH_3)$_2$), 25.7 (*p*-CH(*C*H$_3$)$_2$), 25.4 (*o*-CH(*C*H$_3$)$_2$), 24.4 (*o*-CH(*C*H$_3$)$_2$); IR (Nujol): ν/cm^{-1} 1755(w), 1600(m), 1555(m), 1545(m), 1530(w), 1235(sh), 1180(w), 1125(w), 1075(sh), 1065(w), 1045(w), 870(m), 845(sh), 640(m), 575(w), 530(w); UV/Vis (toluene): λ_{max} = 490 nm, ε = 1500 L mol^{-1} cm^{-1}. **2**: To a red solution of 0.35 g (0.32 mmol) of Ar*GeGeAr* in toluene (10 ml), 0.040 ml (0.35 mmol) of 2,3-dimethyl-1,3-butadiene was added *via* a microsyringe at ambient temperature under vigorous stirring. A few minutes after the addition the color of the reaction mixture faded from deep red to orange. Stirring for an additional 12 h resulted in a colorless solution. The volatile materials were removed under reduced pressure and the white, solid residue was dissolved with hexane (20 ml). The colorless solution was then concentrated to incipient crystallization (*ca.* 10 ml). Storage at 5 °C for 12 h yielded $\mathrm{[Ar^*\overline{Ge\{CH_2C(Me)C(Me)CH}_2\}CH_2C(Me){=}]_2}$ **2**, as large, colorless cubes. The supernatant solution afforded further traces of crystalline **2** along with a pale yellow oil whose exact composition has not been identified. Yield of **2** (M = 1355.19): 0.16 g, 0.12 mmol, 37.5%, mp 249–251 °C (no decomposition). ^{1}H NMR (C_6D_6): δ 7.12–7.19 (m, 14H, *m*-Trip + *p*-C_6H_3, overlap), 2.89 (m, 12H, *p*-C*H*(CH_3)$_2$ + *o*-C*H*(CH_3)$_2$, overlap, ^3J 6.8 Hz), 2.75 (br, 12H, CH_2 butadiene), 1.64 (s, 18H, CH_3 butadiene), 1.32 (d, 12H, *o*-CH(C*H*$_3$)$_2$, ^3J 6.8 Hz), 1.31 (d, 12H, *o*-CH(C*H*$_3$)$_2$, ^3J 6.4 Hz), 1.09 (d, 24H, *p*-CH(C*H*$_3$)$_2$, ^3J 6.8 Hz); ^{13}C NMR (C_6D_6): δ 155.0 (*i*-C_6H_3), 148.7 (*o*-C_6H_3), 147.0 (*o*-Trip), 139.7 (*p*-Trip), 130.0 (*C*Me butadiene), 130.5 (*i*-Trip), 129.6 (*m*-C_6H_3), 129.1 (*p*-C_6H_3), 120.7 (*m*-Trip), 38.8 (CH_2 butadiene), 34.9 (*p*-*C*H(CH_3)$_2$), 31.0 (*o*-*C*H(CH_3)$_2$), 27.2 (*p*-CH(*C*H$_3$)$_2$), 26.0 (*o*-CH(*C*H$_3$)$_2$), 24.5 (*o*-CH(*C*H$_3$)$_2$), 19.2 (CH_3 butadiene); IR (Nujol): ν/cm^{-1} 1925(w), 1870(w), 1760(w), 1590(m), 1575(m), 1555(m), 1530(w), 1320(sh), 1055(m), 750(m), 660(sh), 600(w), 575(w), 560(w). Compounds **1** and **2** gave satisfactory C,H analysis.

‡ *Crystal data* for **2** at 90 K with Mo-Kα radiation (λ = 0.71073 Å): $C_{90}H_{128}Ge_2$, M = 1355.19, colorless cube, monoclinic, space group $P2_1/c$, a = 12.8612(8), b = 19.4797(12), c = 16.8275(10) Å, β = 106.8280(10)°, Z = 4, D_c = 1.115 g cm^{-1}, μ = 0.787 mm^{-1}, R_1 = 0.0671 for 5196 [$I > 2\sigma(I)$] data. CCDC reference number 185422. See http://www.rsc.org/suppdata/cc/b2/b203403d/ for crystallographic data in CIF or other electronic format.

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