Reduction of $Ge(Cl)C_6H_3mes_2$-2,6 to give the cyclotrigermenyl radical $(GeC_6H_3mes_2\text{-}2,6)_3^{\bullet}$ and the trigermenyl anion salt $K(GeC_6H_3mes_2\text{-}2,6)_3$

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Treatment of $Ge(Cl)C_6H_3mes_2$-2,6 1 with 1 equiv. of KC_8 furnishes the new cyclotrigermenyl radical $(GeC_6H_3mes_2\text{-}2,6)_3^{\bullet}$, 2) which is characterized by EPR and X-ray crystallography; reduction with a further equivalent of KC_8 gives the new trigermenyl allyl anion analogue $K(GeC_6H_3mes_2\text{-}2,6)_3$ which has an open Ge_3 framework with a wide Ge–Ge–Ge angle of 159.19(10)°at the central Ge and a Ge–Ge distance of 2.422(2) Å.

Recent reports have shown that sterically crowding ligands with terphenyl substituents can stabilize coordination and bonding not readily observed with other ligands. Prominent examples include low-coordinate metal thiolates such as the monomeric $Fe(SC_6H_3mes_2\text{-}2,6)_2$[1] (mes = $C_6H_2Me_3$-2,4,6), the formally aromatic cyclotrigallane $M_3(GaC_6H_3mes_2\text{-}2,6)_3$ (M = Na[2a] or K[2b]), or the germylyne complex $(\eta^5\text{-}C_5H_5)(CO)_2MoGeC_6H_3$-mes$_2$-2,6 featuring a MoGe triple bond.[3] The synthesis of the latter species by the reaction of $Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$[4] with $Ge(Cl)C_6H_3mes_2$-2,6, **1**,[5] has prompted further investigation of the chemistry of the $Ge(Cl)C_6H_3mes_2$-2,6 species. Here, its reduction to form either the neutral radical $(GeC_6H_3mes_2\text{-}2,6)_3^{\bullet}$, which has a three-membered Ge_3 ring, or the salt $K(GeC_6H_3mes_2\text{-}2,6)_3$, with an open Ge_3 core structure, is described.

Treatment of $Ge(Cl)C_6H_3mes_2$-2,6, **1**,[5] with slightly less than 1 equiv. of KC_8[6] affords the radical $(GeC_6H_3mes_2\text{-}2,6)_3^{\bullet}$ **2**, as dark blue crystals in moderate yield.† In a similar manner, the addition of excess KC_8 (2 equiv. per germanium) gives the anionic trigermanium species $(GeC_6H_3mes_2\text{-}2,6)_3^-$ as its potassium salt $K(GeC_6H_3mes_2\text{-}2,6)$, **3**, which was isolated as dark green crystals.

The structures of both **2** and **3** have been determined by X-ray crystallography.‡ The data for **2** showed that it crystallizes as crystallographically independent trimeric units which feature a cyclic triangular arrangement of three germaniums (Fig. 1) in which the average Ge–Ge distance is 2.35(7) Å. Unfortunately, the structure displayed disorder problems involving the important core atoms, which adopt a number of slightly different positions such that several plausible Ge_3 triangular arrays are possible which leave the organic ligand atoms unmoved. Nonetheless, the structure could be refined to an overall residual (R_1) value of 0.064. The presence of a disordered core unit is consistent with the formulation of **2** as a substituted cyclogermenyl radical (*i.e.* a germanium analogue of a cyclopropenyl radical). In valence bond terms, the ring in such a species is expected to involve a double bond between two members with the unpaired electron located on the remaining atom. Thus, three orientations (**A**, **B**, **C**) may be written since each germanium bears the same $C_6H_3mes_2$-2,6 substituent.

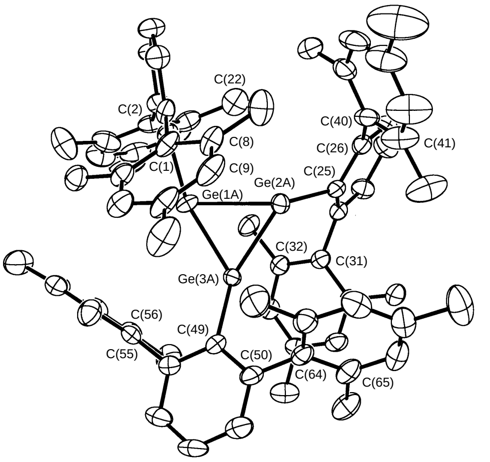
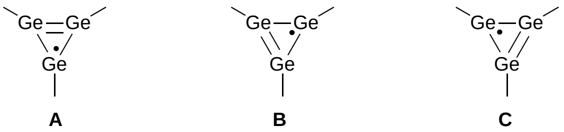


Fig. 1 Crystal strucutre of **2** featuring one possible arrangmeent of the Ge_3 core. The average Ge–Ge distance is 2.35(7) Å.



The EPR spectrum of **2** in hexane solution at room temp. displays a major signal with g = 2.0069 and has a hyperfine coupling to a single ^{73}Ge (I = 9/2, 7.8% natural abundance) nucleus. The relative intensity of the hyperfine lines in the EPR spectrum is consistent with the location of the unpaired electron on one germanium atom. The π-molecular orbital picture of the ring features a molecular orbital of a symmetry occupied by a pair of electrons and the doubly degenerate e antibonding level occupied by the unpaired electron. The relatively low hyperfine coupling, a (^{73}Ge) = 16 G, is consistent with the location of the unpaired electron in an orbital of π-symmetry indicating planar or near-planar geometry at the germanium center.

Treatment of **1** with 2 equiv. of KC_8[6] affords the anionic species **3** (Fig. 2) as its potassium salt. Apparently, the addition of a further electron to **2** results in the opening of the Ge_3 ring to afford a trigermenyl analogue of the allyl anion (Scheme 1).

The structure of **3** is characterized by a two-fold rotation axis of symmetry along the C(1)–Ge(1) axis implying planar geometry at Ge(1). The torsion angle between the C(1) ring and the coordination plane at Ge(1) is 81.2°. The potassium countercation is complexed in a π fashion by the C(5) (K–centroid 2.68 Å) and C(20) (K–centroid 2.84 Å) mesityl rings and occupies the two possible coordination sites with equal probability (*i.e.* 50% occupancy of each site). The complexing mesityl rings form a bent sandwich structure at the K^+ ion which also interacts very closely with a methyl group [$K^+\cdots$C(35) 2.81Å] from the C(29) methyl ring. The $K^+\cdot\cdot\pi$-interactions are at the lower end of the range previously observed [*cf.* K–C range 3.142(5)–3.253(4) Å and K–centroid of 2.87 Å in (pmdeta)(thf)$KCPh_3$;[7] K–C 3.167(2)–3.288(2) Å in $\{(pmdeta)KCH_2Ph_{\infty}\}$.[8]]. The Ge_3 array is characterized by a wide Ge(2)–Ge(1)–Ge(2a) angle of 159.19(10) Å and a Ge(1)–Ge(2) distance of 2.422(2) Å. The Ge(1)–C(1) and Ge(2)–C(14) distances are 2.048(14) and 2.022(10) Å. In addition, the Ge(1)–Ge(2)–C(14) angle is

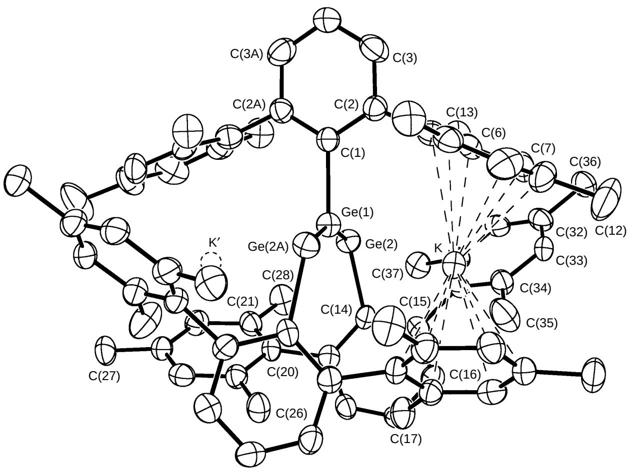
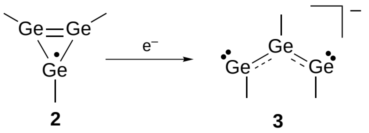


Fig. 2 Crystal structure of **3**. The 50% K$^+$ occupancy of each site is indicated by displaying only one set of K$^+$ mesityl interactions. Some important bond distances (Å) and angles (°) are: Ge(1)–Ge(2) 2.422(2), Ge(2)–Ge(1)–Ge(2A) 159.19(10), Ge(1)–Ge(2)–C(14) 111.3(3). Further data are given in the text.



Scheme 1

111.3(3)° and there is a torsion angle of 20.6° in the C(14)–Ge(2)···Ge(2a)–C(14a) array. These geometrical features are consistent with the description of the (GeC$_6$H$_3$mes$_2$-2,6)$_3^-$ ion as an allyl anion analogue in which the (*Z*-oriented) lone pairs of the two outer germaniums behave as phantom ligands.

In many respects the structures of **2** and **3** complement that of the recently reported cyclotrigermenium cation [GeSiBu$^t_3$]$_3^+$ **4**[9] which has a formally aromatic 2π-electron system with an average Ge–Ge bond distance of 2.326(4) Å, *cf.* Ge–Ge double bond distance of 2.239(4) Å in the Ge$_3$ ring species *c*-[{GeSiBu$^t_3$}$_2${Ge(SiBu$^t_3$)$_2$}].[10] The addition of a further electron may afford a neutral cyclotrigermenyl radical species exemplified by **2**, which contains an unpaired electron in a doubly degenerate antibonding π orbital. The average Ge–Ge bond length observed in **2** is 2.327(12) Å which is very similar to that in **4** and *ca.* 0.1 Å shorter than a normal Ge–Ge single bond, 2.44 Å.[11] However, the large standard deviations in the structural parameters of **2**, as well as the different type of substituent, make such a comparison of limited value. Further reduction of **2** affords **3**. Presumably, the addition of a second electron to **2** results in sufficient destabilization of the structure to effect its rearrangement to give **3**. In MO terms the HOMO in the open structure is non-bonding rather than antibonding as it would be if the ring structure were retained. The average Ge–Ge bond length in **3** is *ca.* 0.1 Å longer than that seen in **4**. It is probable that the increased interelectronic repulsion owing to the negative charge, coupled with the 20.6° torsion angle between the planes at Ge(2) and Ge(2a), contributes to the lengthening of the Ge–Ge bonds which are only marginally shorter than a normal Ge–Ge single bond.[11] Further investigation of the chemical and spectroscopic properties of **2** and **3** and their tin analogues is in progress.

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Footnotes and References

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† All manipulations were carried out under anaerobic and anhydrous conditions. The compound Ge(Cl)C$_6$H$_3$mes$_2$-2,6,[5] which exists as Ge–Ge bonded dimer in the solid, and KC$_8$ [6] were synthesized as described in the literature.

2·0.5thf. To a well stirred solution of **1** (0.42 g, 1.0 mmol) in thf (15 ml) was added KC$_8$ (0.135 g, 0.85 mmol) *via* a solids-addition tube. The solution which was initially yellow became a very dark red, almost black, color. After 3 h all the KC$_8$ appeared to have been consumed, whereupon the volatile materials were removed under reduced pressure. The black residue was extracted with hexane (2×20 ml) and the solution was filtered through Celite. The volume was reduced to *ca.* 20 ml and the solution was placed in a −20 °C freezer for 4 days to afford a mixture of a minor amount of microcrystalline orange crystals (*i.e.* **1**) together with large dark blue, almost black, crystals which could be easily separated by suspending the microcrystals in the solution and decanting rapidly with a cannula to afford X-ray quality crystals of **2**·thf [mp > 100 °C (decomp.)]. Yield 0.13 g, 28.5%. The thf in **2**·0.5thf may be removed by prolonged (12 h) pumping at 0.01 mmHg.

3·0.5C$_6$H$_{14}$, LiC$_6$H$_3$mes$_2$-2,6[12] (1.2 g, 3.73 mmol) was added *via* a solids-addition funnel to GeCl$_2$·dioxane (0.86 g, 3.73 mmol) in thf (30 ml) and stirred for 3 h. KC$_8$ (1.01 g, 7.4 mmol) was then added *via* a solids-addition funnel and the mixture was stirred for a further 2 h. The volatile materials were then removed under reduced pressure and the residue was extracted with 30 ml of hexane–toluene (4 : 1). The solution was filtered through Celite and concentrated to *ca.* 20 ml. Storage of 2 days in a −20 °C freezer afforded the product **3** as dark green crystals. Yield 0.35 g, 0.29 mmol, 23.5%. Mp 180–2 °C, ^{1}H NMR(C$_7$D$_8$) δ 2.02 (s, 24H, *o*-CH$_3$), 2.03 (s, 12H, *o*-CH$_3$), 2.21 (s, 6H, *p*-CH$_3$), 2.26 (s, 12H, *p*-CH$_3$), 6.63 (s, 8H, *m*-mes), 6.767 (d, 6H, J_{HH} 6.9 Hz), 6.84 (s, 4H, m-mes), 7.08 (t, 3H, J_{HH} 7.0 Hz), *p*-C$_6$H$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 21.16, 22.69 (*o*-CH$_3$), 22.89, 23.19 (*p*-CH$_3$), 135.02, 135.82, 130.45, 137.96, 138.55, 139.14, 139.62, 141.18, 142.19, 143.23, 143.91, 145.55, 145.85 (aryl). UV–VIS (λ_{max}, ε: 266 nm, ε = 7000 dm^3 mol^{-1} cm^{-1}).

‡ *Crystal data* for **2**·0.5thf and **3** (T = 130 K, Cu-Kα = 1.54178Å): **2**·0.5thf, C$_{74}$H$_{79}$GeO$_{0.5}$, M = 1194.14, monoclinic, space group $C2/c$, a = 43.284 (5), b = 12.921(2), c = 22.746(3) Å, β = 102.78(1)°, V = 12 435(3) Å^3, abs. coeff. = 2.022 mm^{-1}, Z = 8, wR_2 = 0.1756 for all 8408 data, R_1 = 0.064 for 6387 [$I > 2\sigma(I)$] data.

3.0.5 C$_6$H$_{14}$, C$_{75}$H$_{82}$Ge$_3$K, M = 1240.28, monoclinic, space group $C2/c$, a = 17.865(6), b = 17.994(5), c = 23.323(9) Å, β = 108.06(3)°, V = 71 284 Å^3, abs. coeff. = 2.288 mm^{-1}, Z = 4, wR_2 = 0.2453 for all 4665 data, R_1 = 0.09 for 3170 [$I > 2\sigma(I)$] data. CCDC 182/523.

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