Lewis base induced tuning of the Ge-Ge bond order in a "digermyne"

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The reaction of the "digermyne" Ar'GeGeAr' (Ar' = $C_6H_{3^{-2},6}(C_6H_3-2,6-Pr_2)_2$; Ge-Ge = 2.2850(6) Å) with mesityl isocyanide affords the bis adduct [Ar'GeGeAr'(CNMes)_2] which results in the conversion of a Ge-Ge multiple bond to a long Ge-Ge single bond (= 2.6626(8) Å).

Stable homonuclear alkyne analogues of all the heavier group 14 elements have now been isolated and characterized.^{1–8} They have the general formula REER (E = Si, Ge, Sn, Pb; R = bulky aryl or silyl ligand) and display strongly *trans*-bent geometries and bond orders that are less than three because of increasing lone pair character at the group 14 element as the group is descended. For the heaviest element, lead, the element–element bond is essentially single, as shown in C,^{1.9} where **A** represents a triple bond, as found in acetylene and its derivatives. For the silicon, germanium and tin analogues, the bonding lies somewhere between these two extremes, as illustrated by the canonical form **B**.^{10–12}



A consequence of the bent geometry is that electron density is removed from the bonding region so that the EE unit becomes increasingly electron poor in contrast to the electron rich alkynes. We have shown that Ar'GeGeAr' (1, Ar' = C_6H_3 –2,6(C_6H_3 –2,6- $Pr_2^i_{2}$), Scheme 1) displays high reactivity toward a variety of electron rich unsaturated molecules and many of these reactions have led to complete cleavage of the Ge–Ge bond.^{13–17} Uniquely, however, the reaction of ^tBuNC with Ar'GeGeAr' afforded a 1 : 1 adduct, Ar'GeGeAr'·CNBu^t (2), in which the isonitrile was coordinated to one of the Ge centers.¹⁶

The coordination of the ^tBuNC donor occurred in the plane of the C(ipso)GeGeC(*ipso*) core and the GeGe distance in **2**



Scheme 1 Reactivity of Ar'GeGeAr' toward ^tBuNC or MesNC.

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 $(2.3432 \text{ Å})^{16}$ increased slightly relative to that in 1 (2.2850(6) Å).³ This is consistent with the retention of the GeGe multiple bond as illustrated in 2 (Scheme 1). This behavior can be accounted for by reference to Fig. 1, which shows that there is a change in the frontier orbitals for the heavier derivatives with bent geometry.^{18,19} The new arrangement differs from the familiar 2π (HOMO)- $2\pi^*$ (LUMO) pattern in alkynes as a result of a second order Jahn– Teller mixing of a σ^* -orbital and the in-plane π -orbital (both of which have b_u symmetry in the C_{2h} point group) to afford n_+ and n- non-bonding orbitals. This occurs because of weaker E-E bonding and the resultant smaller energy separation, and hence a stronger interaction, between the molecular energy levels. The HOMO remains a π -orbital (a_u symmetry) whereas the LUMO is an n+ non-bonding orbital of ag symmetry. Thus, the Lewis base ^tBuNC interacts with the unoccupied $a_g(n_+)$ orbital. This interaction stabilizes n+ but diminishes the overlap between the two Ge centers slightly.[†]

According to Fig. 1, the reaction with the second Lewis base molecule should result in addition to the next available Ge–Ge π^* level, leading to substantial lengthening of the Ge–Ge bond. The synthesis of such an adduct has not been reported for any heavier alkyne analogues and the addition of excess ¹BuNC to Ar'GeGeAr' does not result in the isolation of a product incorporating more than one isonitrile unit.¹⁶ We now report that the reaction of Ar'GeGeAr' with MesNC (Mes = C₆H₂–2,4,6-Me₃) yields the bis adduct **3** (Scheme 1), which is characterized by a very long Ge–Ge bond.



Fig. 1 Selected orbital interactions in the C_{2h} symmetric *trans*-bent REER molecule. The opposite phases for s- and p-orbitals are indicated by black and gray shading respectively.

The complex **3** was obtained as dark red crystals by the addition of two equivalents of MesNC to a solution of Ar'GeGeAr' in hexane.[‡] The X-ray crystal structure§ of **3** is illustrated in Fig. 2 where it can be seen that each germanium is complexed by a MesNC: donor. As a result, the germaniums are pyramidally coordinated with interligand angular sums at Ge1 = 293.2(2)° and Ge2 = 292.5(2)°. The Ge–C distances to both the MesNC: and Ar' ligands are very similar and lie in the narrow range 1.996(5)– 2.033(4) Å. The Ge1–Ge2 bond length is 2.6626(8) Å. There is a torsion angle of 104.4° in the C1–Ge1–Ge2–C31 unit of the Ar'GeGeAr' array and the torsion angle involving the two isonitrile units, *i.e.* C61–Ge1–Ge2–C71, is 55°. The N1–C61 and N2–C71 distances within the isonitrile donors are 1.145(6) and 1.157(6) Å, with bending angles of 159.5(5)° at the ligating carbons of each ligand.

The Ge1–C61 and Ge2–C71 bonds subtend to almost right angles (average 88.3°) with respect to the Ge–Ge bond. Inspection of Fig. 2 shows that the mesityl rings of the MesNC ligands are essentially parallel to each other. The ring planes are separated by *ca.* 3.5 Å. However, the two rings have staggered geometries with respect to each other and the π -interactions appear to be weak.

At ambient temperature the ¹H NMR spectrum of **3** is complicated but shows only one mesityl environment with singlet resonances at 1.99, 2.13 and 6.48 ppm. The isopropyl region consists of three overlapping methyl environments at 1.14 ppm and one further downfield at 1.50 ppm, with a similarly complicated region corresponding to the methine environments at 2.79–3.27 ppm, suggesting hindered rotation around the Ge–Ge



bond and of the flanking rings of the terphenyl ligands. At elevated temperature in d_8 -toluene the spectrum simplifies to two isopropyl environments, indicated by four doublets at 1.05, 1.14, 1.27 and 1.50 ppm, and two septets at 2.73 and 3.18 ppm (CH groups). The IR spectrum displays a CN stretching absorption at 2113 cm⁻¹.

The ca. 0.38 Å lengthening of the GeGe bond upon coordination of 1 by two MesNC molecules is the most notable feature of the structure of 3. It stands in contrast to the slight increase observed upon coordination of a single isonitrile in 2 and is indicative of significantly greater Ge-Ge bonding changes. It seems probable that, unlike ^tBuNC, the addition of two equivalents of MesNC can occur because the MesNC has a flat, two-dimensional shape and the mesityl rings can be oriented parallel to each other without undue steric repulsion. Thus, the steric congestion between the isonitriles can be minimized for the MesNC groups by parallel ring orientation but this cannot occur in the case of ^tBuNC because of the steric pressure of the bulky ^tBu substituents. In addition, the mesityl substituents are partially eclipsed since the two isonitriles complex on the same side of the molecule with only a 55° torsion angle between them. This also results in a decrease in the 180° torsion angle between the two large Ar' substituents in the precursor, Ar'GeGeAr', to 104.4° in 3. It is notable that the coordination of both isonitriles occurs perpendicularly to the coordination plane at each germanium in the Ar'GeGeAr' unit. Furthermore, the GeGeC(ipso) bending angles in the Ar'GeGeAr' unit have decreased by ca. 23° between 1 and 3. Thus, the Ar'GeGeAr' moiety in 3 is much more strongly transbent than it is in free Ar'GeGeAr'. In effect, the Ge-Ge bond is now a single one and complexation of the MesNC donors takes place perpendicularly to the germanium coordination planes. The Ge–Ge bond is much longer than the *ca*. 2.44 Å distance normally seen in elemental germanium²⁰ or digermanes,²¹ R₃GeGeR₃. The Ge-Ge bond length probably is also increased because the bond is now formed by head-to-head overlap of essentially 4p-orbitals rather than hybrid orbitals as in R₃GeGeR₃ species.

An alternative explanation for the formation of **3** is based on the valence bond description of the more strongly bent skeleton as a bis(germylene) structure, which is illustrated by **C**. In this model, each germanium carries a lone pair in the molecular plane as well as an empty 4p-orbital perpendicular to that plane. The latter are thus available for interaction with two molecules of a Lewis base such as MesNC:. This view is also consistent with recent computational work,^{11,22} where it was shown that the greater bending of the skeleton eventually leads to two non-bonding, lone pair orbitals, n₊ and n₋, with the Ge centers being connected by a single σ -bond as in **C**. The LUMO and LUMO + 1 are now π and π^* levels (see ref. 11 and 22) which can interact with the two isonitrile donors to form complex **3** in which the germaniums are connected by a simple σ -bond, as argued above.

In summary, it has been shown that the "digermyne" Ar'GeGeAr' can form the complex 3 with two Lewis base isonitriles. The structural parameters of 3, the coordination mode of the isonitriles and the fundamental differences in the isonitrile bonding between 2 and 3 have provided experimental insight into the orbital arrangements in these species and Ar'GeGeAr'.

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Notes and references

† Factors that may contribute to the lengthening of the Ge–Ge bond in **2** include an increase in the coordination number at one of the germaniums. In addition, the coordination of ¹BuNC: results in a "freezing out" of the resonating lone pair (*cf.* structure **B**) at the uncomplexed Ge center. This leads to a dramatic reduction in the Ge–Ge–C bending angle,¹⁵ which probably increases the 4p-character of the Ge–Ge σ -bond, which lengthens as a result.

All manipulations were carried out under anaerobic and anhydrous conditions. To a solution of Ar'GeGeAr' (1, Ar' = $C_6H_3-2,6(C_6H_3-2,6-4)$ Prⁱ₂)₂, 0.300 g, 0.320 mmol) in *n*-hexane (50 mL) was added MesNC (0.093 g, 0.640 mmol) in n-hexane (20 mL) at ambient temperature and the mixture was stirred at room temperature for 6 h. The resulting dark red/ purple solution was filtered, concentrated and stored at ca. -18 °C overnight to give dark red/purple crystals of 3 (0.253 g, 64.2%). Mp: 77-79 °C. ¹H NMR (C₆D₆, 300.08 MHz): δ 1.14 (m, 36H, CHMe₂), 1.50 (m, 12H, CHMe₂), 1.99 (s, 6H, Mes), 2.13 (s, 12H, Mes), 2.90 (m, 4H, CHMe₂), 3.23 (sept, 4H, J = 6.6 Hz, CHMe₂), 6.48 (s, 4H, Mes), 7.24 (m, 18H, Ar–H). ¹³C NMR (C₆D₆, 100.52 MHz): δ 18.6 (C=N), 20.9 (Mes), 23.6 (CHMe2), 24.2 (CHMe2), 25.9 (CHMe2), 26.1 (CHMe2), 31.0 (CHMe2), 31.2 (CHMe2), 123.05, 123.25, 123.62, 123.90, 124.03, 128.64, 128.76, 129.09, 129.25, 129.58, 139.01, 141.81, 141.96, 142.13, 142.23, 144.89, 145.48, 145.90, 146.19, 146.64, 146.89, 147.70, 147.82, 151.80, 196.06 (unsaturated carbon). IR (KBr, Nujol): 2113 (m, CN stretch) cm⁻ § Crystal data for 3 at T = 90(2) K with MoK α ($\lambda = 0.71073$ Å): $C_{80}H_{96}Ge_2N_2$, M = 1230.77, monoclinic, space group $P2_1/n$, a =13.141(1) Å, b = 21.235(2) Å, c = 24.860(2) Å, $\beta = 97.467(2)^{\circ}$, U = 101 101 101 102 1023 $(I > 2\sigma(I))$ reflections, wR2 = 0.1478 (all data). CCDC 618885. For crystallographic data in CIF or other electronic format see DOI: 10.1039/ b612202g

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