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Synthesis and Characterization of a Digermanium Analogue of an Alkyne**

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The heavier Group 14 element analogues of alkynes, in which one or both carbon atoms of the triple bond are replaced by silicon, germanium, tin, or lead, are a unique compound class that has attracted considerable discussion and interest.[1, 2] Over the last decade, a rapidly growing series of computational papers[3–26] have predicted a *trans*-bent structure[27] for heavier-element analogues that carry organic substituents.[16–26] With the exception of the lead compound 2,6-Trip$_2$H$_3$C$_6$PbPbC$_6$H$_3$-2,6-Trip$_2$ (Trip = C$_6$H$_2$-2,4,6-*i*Pr$_3$),[28] which has a planar, *trans*-bent CPbPbC core (Pb-Pb-C = 94.26(4)° and a long, essentially single Pb–Pb bond (Pb–Pb = 3.1881(1) Å),[14, 28] no stable Group 14–Group 14 heavier analogues of alkynes have been described. Various experiments[29–34] have indicated the existence of alkyne-like transient species but none of these has been isolated and no structural details are available. The synthesis, structural characterization, and reaction chemistry of such compounds would provide valuable bonding information, especially in view of the current debate on the nature of multiple bonds between heavier main group elements.[35–39] An additional feature of interest is that these potentially triple-bonded systems have been described as "a final challenge" in the area of main-group multiple bonding.[2] The isolation and structural characterization of a germanium alkyne analogue 2,6-Dipp$_2$H$_3$C$_6$GeGeC$_6$H$_3$-2,6-Dipp$_2$ (**1**; Dipp = C$_6$H$_3$-2,6-*i*Pr$_2$) are now described.

2,6-Dipp$_2$H$_3$C$_6$GeGeC$_6$H$_3$-2,6-Dipp$_2$ **1**

Compound **1** was synthesized by the reaction of Ge(Cl)C$_6$H$_3$-2,6-Dipp$_2$ with potassium in THF or benzene. It was isolated as orange-red crystals which were characterized by ^{1}H and ^{13}C NMR, IR, and UV/Vis spectroscopy and by single-crystal X-ray crystallography.[40] The UV/Vis spectrum displays three relatively intense absorptions at 280, 371, and 501 nm which may be the result of $\pi-\pi^*$ and $n-\pi^*$ transitions. The X-ray structure revealed a centrosymmetric molecule (Figure 1) that has a planar *trans*-bent C1-Ge1-Ge1A-C1A core array as required by symmetry. The Ge1–Ge1A and Ge1–C1 bond lengths are 2.2850(6) and 1.996(3) Å, and the Ge1-Ge1A-C1A angle is 128.67(8)°. The central aryl ring of the terphenyl ligand is essentially coplanar (torsion angle 0.4°) with the C1-Ge1-Ge1A-C1A array, and the planes of the flanking aryl rings are oriented at approximately 82° with respect to the central aryl ring. The Ge1-C1-C2 and Ge1-C1-C6 angles differ by 7.7° and there is a 4.0° angle between the Ge1-C1 bond and the C1 ⋯ C4 vector. A cyclic voltammogram of the compound in THF solution displays a reduction wave at −1.38 V and an oxidation at +0.7 V versus the saturated calomel electrode (SCE).

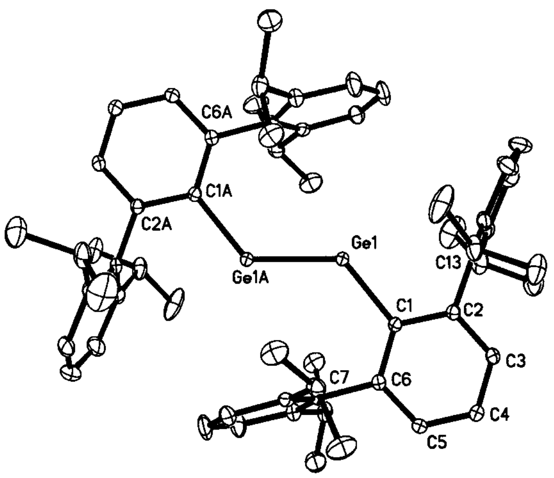

Figure 1. ORTEP plot of **1**, thermal ellipsoids set at 30% probability, H atoms are not shown. Selected bond lengths [Å] and angles [°]. Ge1-Ge1A 2.2850(6), Ge1-C1 1.996(3), C1-C2 1.412(4), C1-C6 1.408(4); Ge1A-Ge1-C1 128.67(8), Ge1-C1-C2 116.9(2), Ge1-C1-C6 124.6(2), C1-C2-C6 118.5(3).

Compound **1** is a stable digermanium analogue of an alkyne. The Ge–Ge distance is considerably shorter than a normal Ge–Ge single bond (ca. 2.44 Å)[41] and indicates the presence of considerable multiple-bonding character. The

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Ge–Ge distance is in the shorter half of the known range (2.21–2.46 Å) for digermenes—the digermanium analogues of alkenes.[42, 43] The most sterically related digermene is the compound 2,6-$Trip_2H_3C_6(Me)GeGe(Me)C_6H_3$-2,6-$Trip_2$[43] which has Ge–Ge and Ge–C (aryl) distances of 2.3173(3) Å and 1.971(2) Å. On this basis it could be argued that the Ge–Ge bond order in **1** is approximately two—a conclusion that receives support from some calculations.[7] The bending is a consequence of an accumulation of nonbonding electron density at the germanium atoms that is indicative of incipient lone-pair formation.[27] As a result, the Ge–Ge bond strength and order is decreased from idealized triple bonding.[44] Nonetheless, models of RGeGeR species have been described as "digermynes" and as being triply bonded.[5, 10, 45] The chemistry of **1** should reflect the decreased Ge–Ge bond strength and the lone-pair character at the germanium centers.[46]

The structure of **1** may also be compared with those calculated[10] for the closely related, but structurally uncharacterized, derivative **2** which differs only in that it possesses *para-i*Pr substituents on the flanking aryl rings and for the simpler aryl species PhGeGePh.[13]

2,6-$Trip_2H_3C_6GeGeC_6H_3$-2,6-$Trip_2$ **2**

The calculations for **2** afforded an optimized structure with a Ge–Ge distance of 2.277 Å whereas a shorter Ge–Ge bond length of 2.25 Å was calculated for PhGeGePh. These values are in reasonable agreement with the experimentally observed 2.2850(6) Å in **1**. In contrast, the calculated Ge-Ge-C *trans*-bending angle of 123.2° and torsion angle of 22.4° between the germanium coordination planes in **2** differ from the measured values in **1**. In addition, the central aryl rings of the terphenyl groups of the optimized structure of **2** were calculated to be almost perpendicular to the CGeGeC core. The differences between the observed structure of **1** and the calculated structure of **2** underline the important effects of *para-i*Pr substituents of the flanking rings. The coplanarity of the central aryl rings with the CGeGeC array in **1** suggests conjugation between the Ge–Ge multiple bond and the arene. However, the Ge–C distance in **1**, 1.996(3) Å, lies in the range found for terphenyl substituted digermenes (1.971(2)–2.00(6) Å) where conjugation is precluded by high torsion angles.[43] The structure of **1** emphasizes the large effects that substituents on the periphery of the molecule can have on the molecular configuration. This effect is the key to the successful characterization of a "digermyne". Although the name "digermyne" suggests Ge–Ge triple bonding, a triple bond is present only in the linear, less stable configuration.[7] The bond order in **1** is lower than three owing to the *trans*-bending and the length of the Ge–Ge bond. Bond-order calculations for the *trans*-bent ground-state structures of the model compounds afford the bond order and bond length values: MeGeGeMe (2.097, Ge–Ge = 2.197 Å;[10] 2.10, Ge–Ge = 2.24 Å[15]), PhGeGePh (1.74, Ge–Ge = 2.24 Å[15]).

Experimental Section

Under anaerobic and anhydrous conditions an orange solution of Ge(Cl)C_6H_3-2,6-$Dipp_2$[47] (0.79 g, 1.57 mmol) in THF (10 mL) was added to finely divided potassium (0.064 g, 1.65 mmol; ca. 5% excess) in THF (30 mL) at ambient temperature under vigorous stirring. After around 2 h the reaction mixture began to turn red, and upon stirring for 24 h the solution had become deep red. The THF was removed under reduced pressure and the red solid residue was redissolved in hexane (30 mL). The potassium chloride precipitate and any remaining potassium was allowed to settle and the supernatant solution was removed by decantation. The deep red solution was then concentrated to incipient crystallization (ca. 15 mL). Storage at 5°C for 12 h yielded the product **1** as carmine red-orange crystals. Yield: 0.28 g, 38%; m.p. 214–216°C (turns dark red/black after melting); Correct C, H analysis; ^1H NMR (C_6D_6, 399.77 MHz, 25°C): δ = 1.05 (d, $^3J_{H,H}$ = 6.8 Hz, 24H; *o*-CH(CH_3)$_2$), 1.30 (d, $^3J_{H,H}$ = 6.8 Hz, 24H; *o*-CH(CH_3)$_2$), 2.72 (sept, $^3J_{H,H}$ = 6.8 Hz, 8H; *o*-CH(CH_3)$_2$), 6.91 (d, $^3J_{H,H}$ = 7.2 Hz, 4H; *m*-C_6H_3), 7.09 (d, $^3J_{H,H}$ = 8.0 Hz, 8H; *m*-Dipp), 7.18 (t, $^3J_{H,H}$ = 7.2 Hz, 2H; *p*-C_6H_3), 7.29 ppm (t, $^3J_{H,H}$ = 8.0 Hz, 4H; *p*-Dipp); ^{13}C {^1H} NMR (C_6D_6, 100.59 MHz, 25°C): δ = 25.59 (*o*-CH(CH_3)$_2$), 26.06 (*o*-CH(CH_3)$_2$), 31.59 (*o*-CH(CH_3)$_2$), 124.58 (*m*-Dipp), 127.28 (*p*-C_6H_3), 130.024 (*m*-C_6H_3), 141.36 (*p*-Dipp), 145.67 (*i*-Dipp), 146.81 (*i*-C_6H_3), 147.29 (*o*-Dipp), 158.76 ppm (*o*-C_6H_3); IR (nujol): $\tilde{\nu}$ = 1925(w), 1885(w), 1590(w), 1570(2), 1550(w), 1325(sh), 1055(m), 750(m), 450(w), 320(w) cm^{-1}; UV/Vis (hexanes): λ_{max}, ε($L\,mol^{-1}\,cm^{-1}$): 501 (7,500), 371 (34,000), 280 nm (28,000).

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A Cascade Cycloaddition Strategy Leading to the Total Synthesis of (−)-FR182877**

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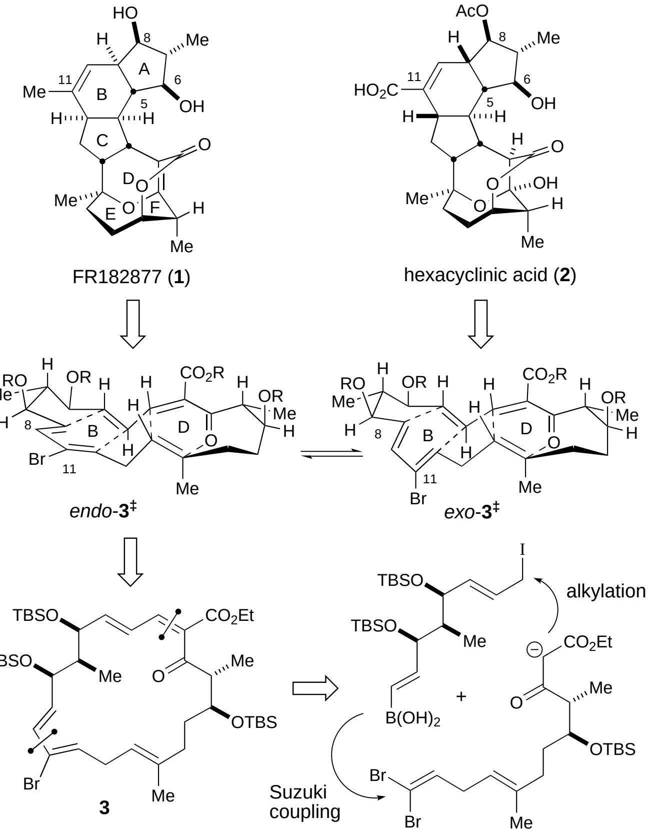
Herein we outline a general strategy for the synthesis of the closely related natural products FR182877 (**1**)[1] and hexacyclinic acid (**2**)[2] from a common macrocyclic precursor (**3**) by a sequence of transannular [4+2] cycloadditions (Scheme 1).[3, 4] This approach has been validated by its successful application to the enantioselective synthesis of (−)-FR182877, and provided confirmation of its assigned absolute configuration.

The cytotoxic substance FR182877 (**1**) was isolated from *Streptomyces* sp. No. 9885 in 1998, and at that time was reported as the enantiomer to the illustrated structure (Scheme 1).[1a] FR182877 exhibits microtubule stabilizing



Scheme 1. FR182877 and hexacyclinic acid retrosynthesis.

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.